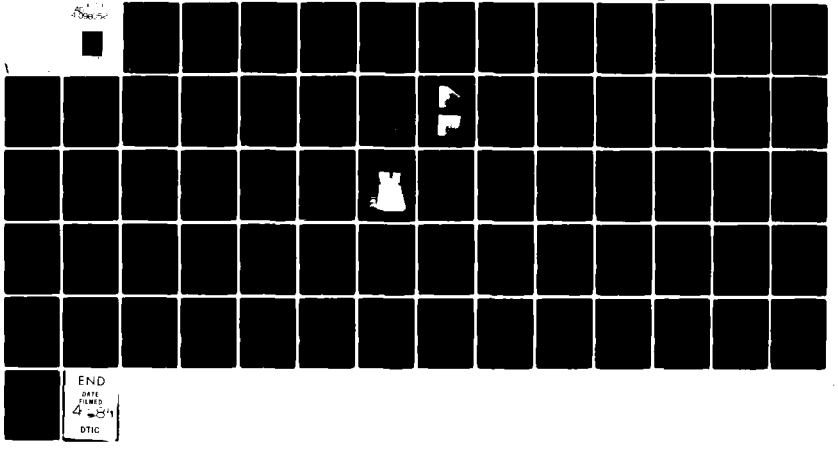
AD-A096 052 ASHLAND CHEMICAL CO COLUMBUS OH F/G 10/2
RADIOTRACER EVALUATION OF THE CONTRIBUTION OF DEGRADATION PRODU--ETC(U)
DEC 80 J T HOGGINS, M L DEVINEY DAAK70-79-C-0020
UNCLASSIFIED 333A-1A NL



END
DATE FILMED
4-81
DTIC

LEVEL II

"RADIOTRACER EVALUATION OF THE CONTRIBUTION OF DEGRADATION PRODUCTS OF PHENOLIC RESINS TO THE POISONING OF ELECTRODES IN THE 190°C HYDROGEN/AIR FUEL CELL"

FINAL TECHNICAL REPORT

DECEMBER, 1980

By

James T. Hoggins

Marvin L. Deviney

U.S. ARMY MOBILITY EQUIPMENT RESEARCH & DEVELOPMENT COMMAND

FORT BELVOIR, VIRGINIA 22060

CONTRACT NO: DAAK70-79-C-0020

ASHLAND CHEMICAL COMPANY
P.O. Box 2219
Columbus, Ohio 43216

NOTICES

DISTRIBUTION STATEMENT

This document has been approved for public release. Its distribution is unlimited.

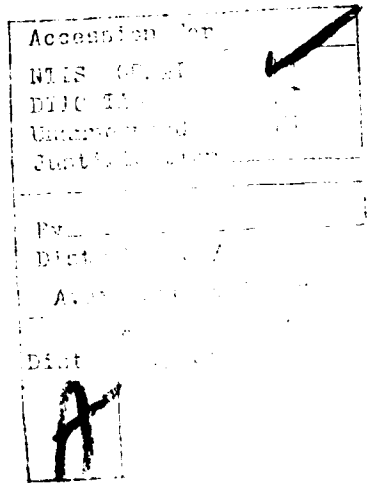
DISCLAIMERS

The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

The citation of trade names and names of manufacturers in this report is not to be construed as official government endorsement or approval of commercial products or services referenced herein.

DISPOSITION

Destroy this report when it is no longer needed. Do not return it to the originator.



SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 3338-18 ✓	2. GOVT ACCESSION NO. AD-A096	3. RECIPIENT'S CATALOG NUMBER 052
4. TITLE (and Subtitle) "Radiotracer Evaluation of the Contribution of Degradation Products of Phenolic Resins to the Poisoning of Electrodes in the 190°C Hydrogen/Air Fuel Cell"		5. TYPE OF REPORT & PERIOD COVERED Final Report March 12, 1979 to Sept. 30, 1980 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) James T. Hoggins Marvin L. Deviney		8. CONTRACT OR GRANT NUMBER(s) DAAK70-79-C-0020
9. PERFORMING ORGANIZATION NAME AND ADDRESS Ashland Chemical Co. (Ventures R&D) P.O. Box 2219 Columbus, Ohio 43216		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 6.37.02A, 1L263702DG10, 03, 014
11. CONTROLLING OFFICE NAME AND ADDRESS U.S. Army Mobility Equipment Research and Development Command Ft. Belvoir, VA 20060		12. REPORT DATE December, 1980 13. NUMBER OF PAGES 60
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office) DCASMA, Dayton c/o Defense Electronics Supply Center Bldg. 5 Dayton, Ohio 45444		15. SECURITY CLASS. (of this report) Unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for Public Release; Distribution Unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Fuel cells, phosphoric acid, bipolar plates, phenolic resins, composite graphite, Carbon-14, radiotracer, electro-catalyst, electrode poisoning, platinum on carbon catalyst, acid-resistant plates

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Improved procedures have been developed for the fabrication of powdered graphite/phenol-formaldehyde resin bipolar plates, which result in greatly improved resistance of the plates to attack by 190°C H_3PO_4. Static ageing tests of graphite-resin composites demonstrated that very low H_3PO_4 corrosion rates could be obtained and that essentially all plate etching occurred during the first 300 hours of test. Two miniature (2" x 2") hydrogen-air fuel cells, with Carbon-14 labelled phenolic resin in the bipolar plates, were successfully operated for 1300 hours each. Post-operation radiochemical analysis showed

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

20. Abstract, cont.
no radioactivity present on the anode or cathode of either cell, thus indicating that phenolic degradation products could not have contributed to any electrocatalyst poisoning during these two runs.

"RADIOTRACER EVALUATION OF THE CONTRIBUTION OF DEGRADATION PRODUCTS OF PHENOLIC RESINS TO THE POISONING OF ELECTRODES IN THE 190°C HYDROGEN/AIR FUEL CELL".

FINAL TECHNICAL REPORT

DECEMBER, 1980

By

James T. Hoggins

Marvin L. Deviney

U.S. ARMY MOBILITY EQUIPMENT RESEARCH & DEVELOPMENT COMMAND

FORT BELVOIR, VIRGINIA 22060

CONTRACT NO: DAAK70-79-C-0020

This document has been approved for public release; its distribution is unlimited.

ASHLAND CHEMICAL COMPANY
P.O. Box 2219
Columbus, Ohio 43216

Incl 1 (Distribution List)

TABLE OF CONTENTS

SUMMARY

The principal objective of this contract program was to develop improved phenol-formaldehyde resin formulations and molding conditions which could be used for the fabrication of corrosion resistant, composite (resin/graphite powder) bipolar plates suitable for prolonged service in H_2-air fuel cells with 190°C phosphoric acid electrolyte. Results obtained in this program demonstrate that Arofene 877LF and A-33 phenolic resins exhibit an especially high degree of resistance to etching by H_3PO_4. Major improvements have been made in the two-step curing/molding process which make possible the fabrication of highly acid-resistant test coupons on a consistent basis. The improved formulation/molding procedure has been successfully applied in the preparation of bipolar plates for 2" x 2" miniature fuel cells.

Two miniature fuel cells, containing bipolar plates with carbon-14 labelled A-33 resin in the H_3PO_4 reservoir area, were successfully operated for 1300 hours. Post-operation radiochemical analysis showed no radioactivity present on the anode or cathode of either cell, and no C-14 was detected in the H_3PO_4 removed from the reservoir and acid-wick. Radiotracer results therefore indicate that phenolic degradation products could not have contributed to any electro-catalyst (Pt/C) poisoning during these two 1300 hour fuel cell runs.

An independent procedure (involving static rather than operational conditions) was used to investigate corrosion of resin/graphite coupons simulating bipolar plates. These tests showed that essentially all corrosion occurred

in the first 300 hours. This means that a 190°C H_3PO_4 pre-treatment of the bipolar plate reservoir before use in a fuel cell can remove resin degradation products, which could be potential poisons.

Work under this contract has led to the development of some new test methods useful for future work. One is a spectrometric method for rapid screening of candidate resins for bipolar plate service in hot H_3PO_4. This means that the costly step of radiochemical synthesis could be deferred until very promising resin systems are found.

I. INTRODUCTION

This report describes the completion of Contract No. DAAK70-79-C-0020, sponsored by the U.S. Army Mobility Equipment Research and Development Command, Ft. Belvoir, Virginia. This program had two principal goals and one "sub-objective". The first objective was to develop improved resin (phenol-formaldehyde) formulation and curing conditions which would make possible the fabrication of resin/graphite composite bipolar plates which would be highly resistant to etching by H_3PO_4 at 190°C (projected operating temperature for the H_2-air fuel cell). The second major objective was to determine if resin impurities or degradation products from the bipolar plates (generated via corrosion by 190°C H_3PO_4) contribute to the poisoning of the carbon-supported platinum electro-catalyst which is used for both anode and cathode in the fuel cell. The sub-objective (to the first major objective) was to investigate potential practical methods for pre-treating cured bipolar plates so that essentially all etchable substances and possible poisons could be removed prior to fuel cell operation.

Past experience, as reported previously [1,2,3], has identified electro-catalyst life and bipolar plate chemical resistivity to hot H_3PO_4, as well as plate mechanical strength and dimensional stability, to be major obstacles to the achievement of the long-term service life goal. Composite bipolar plates, prepared by molding graphite powder with phenol-formaldehyde resin (esp. Novolak-types) binder have been the subject of much study by the Army and its contractors.[4,5,6]

In the operating fuel cell, the bipolar plate serves several functions, which include, briefly, (1) withdrawing of current from one electrode and transference to the adjacent cell, (2) supporting of the electrode sheet, (3) distributing reactant gas to the electrode via ribbed channels, (4) providing a physical barrier so the reactant gases cannot diffuse through and mix, and (5) providing sufficient long term mechanical strength such that compressive forces can be transmitted through the fuel cell stack to maintain good plate to electrode to electrolyte matrix contact.

In an earlier Ashland investigation [7] concerned with fabrication of improved bipolar plates, (1) two promising phenolic resins (Arofene 877LF and A-33) exhibiting high resistance to hot H_3PO_4 corrosion were identified, and (2) a near optimum graphite powder loading for the composite (75 wt %) was established along with a high density blend composition (Asbury graphite powder No. 7101--50%, No. 4015--40% and Micro 250--10%). Also, (3) an improved 2-step molding technique (see Section VII and Appendix I-A) was developed for test coupons (which simulated bipolar plates), resulting in denser, more acid resistant composites. In addition--although not a part of the original contract--(4) a requested cursory radiochemical study was carried out to determine if this approach had potential for monitoring the corrosion of test coupons by 190°C H_3PO_4. For this work, carbon-14 labelled formaldehyde was used to synthesize Arofene 877LF resin containing C-14 in the "methylene bridge" between the phenolic rings. The results from this brief study demonstrated that a significant quantity of radio-labelled material was etched from the test coupons.

The sensitivity of the C-14 technique suggested that it might be useful

for detailed, precise measurements of hot H_3PO_4 etching of a broad range of test coupons prepared using various resins and curing formulations. The C-14 technique also offered the possible opportunity for sensitive monitoring of the migration of resin degradation products from the bipolar plates onto the fuel cell electrodes. Incentives for further work along these lines were considered great enough that authorization was received for a second contract to begin some six months after completion of the first.

II. EXPERIMENTAL APPROACH

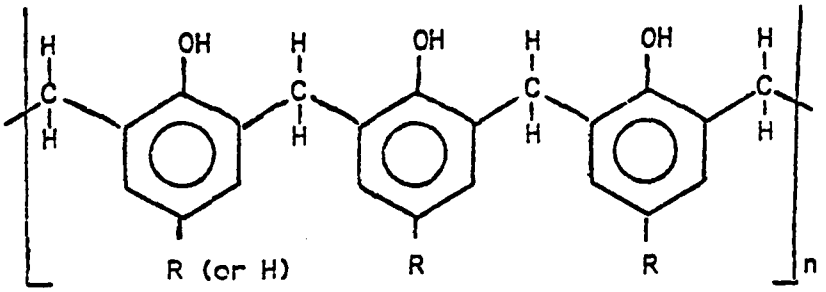
As a brief overview, the experimental program for the present contract consisted of (1) syntheses of the C-14 labelled resins, (2) fabrication of test coupons from labelled resins using the procedures developed in the previous Ashland contract [7], (3) 190°C H_3PO_4 etching of C-14 labelled coupons for both corrosion rate studies and to prepare degradation product "extracts" for subsequent catalyst poisoning studies, (4) preparation of non-radiochemical extracts for fuel cell poisoning studies at Ft. Belvoir, (5) continued formulation/curing work to improve further the hot acid resistance of test coupons, (6) adsorption studies of the Pt/carbon electro-catalyst to determine if the platinum "active" surface could be blocked by resin degradation products, and (7) operation of fuel cells with C-14 labelled bipolar plates to determine if labelled resin degradation products reached the anode or cathode.

Arofene 877LF and A-33 (the latter an experimental resin) were the two phenolic resins selected for radiochemical synthesis and detailed etching/poisoning studies in the new contract program. In addition, the Army asked

that Colloid 8440 phenolic resin be included in the non-radiochemical etching work,and that they be supplied with the resultant degradation product extract.

III. SYNTHESIS OF C-14 LABELLED AROFENE 877LF AND A-33 RESINS

The methylene "bridging" position was chosen as the C-14 labelling position because the "bridge" was considered a likely point of attack (probably leading to polymer chain scission) by hot H_3PO_4.



Schematic Formula of Uncrosslinked Arofene Phenolic Resin

Use of C-14 labelled phenol in the resin synthesis was considered to offer no significant practical advantage in comparison to the plan involving use of C-14 labelled formaldehyde to tag the resin "bridging" position. In addition, formaldehyde-C-14 is considerably less expensive than phenol-C-14. Synthesis of C-14 labelled hexamethylenetetramine for use in resin curing was decided against after some low-etching results were obtained in corrosion studies using resins with C-14 in the "bridge" position.

Some detailed resin purification schemes to remove possible poisons were considered unnecessary because low etching results were obtained with regular non-purified resins early in this study, and because of our adoption of a vacuum-oven post-cure of test specimens. A small amount of work was done, however, with a resin sample which had been steam-stripped to remove excess phenol and volatile reaction by-products.

Non-labelled batches of Arofene 877LF and A-33 resins were initially prepared as "controls" to insure that proper reaction conditions were established so that--on subsequent syntheses using C-14 labelled formaldehyde--resin specifications for physical and curing properties would be met.

The laboratory synthesis procedures used were scaled down versions of commercial Ashland procedures. About 700 grams of resin was synthesized in each batch. The only significant synthesis modification was the addition of the C-14 labelled formaldehyde earlier, and at a lower temperature, than the main HCHO charge. The purpose of this modification was to minimize volatility losses and insure complete utilization of the C-14 labelled HCHO. Radiochemical yields were about 90%.

The physical property data on the Arofene 877LF and A-33 resins related to the present study are presented in Tables I and II, respectively. The test methods used were all ASTM procedures.

TABLE I

Arofene 877LF

Physical Properties Data Summary

Sample Designation	Melt Point (°C)	150°C Melt Time (Sec.)	125°C Flow Time* (Min.)	150°C Cure Time * (Sec.)
3672-102 (Lab. Prep., Control)	95	161	42	68
3672-103 (Lab. Prep., C-14 Labelled)	92	165	44	73
7198F (Plant Batch) **	78	140	52	72
Specifications: Arofene 877LF	75-80	150-165	35-45	65-95
Specifications: Arofene 877	80-95	155-180	25-40	60-90

* Determined with 10% hexamethylenetetramine added to resin.

**Plant batch used in previous Ashland Contract [7]. Also batch used in 190°C H_3PO_4 etching work to prepare resin degradation extracts for Ft. Belvoir.

TABLE II

Arofene A-33

Physical Properties Data

Sample Designation	Melt Point (°C)	150°C Melt Time (Sec.)	125°C Flow Time * (Min.)	150°C Cure * (Sec.)
7214 (Pilot Plant)**	77	264	50	114
3717-32 (Lab. Prep.-Control)	75	229	45	144
3717-40 (Lab. Prep.-Control)	76	253	26	152
3717-45 (Lab. Prep.-C-14 Labelled)	76	256	25	154

* Determined with 10% hexamethylenetetramine added to resin.

** Experimental resin which has not been prepared on larger than pilot plant scale. A-33 specifications are based on this batch, which was also the batch used in previous Ashland Contract [7], and in present work to prepare resin degradation extracts for Ft. Belvoir.

The radiotracer labelled resins listed were the resins used in the 190°C H_3PO_4 etching studies and in the bipolar plates used in the fuel cell operating runs (See Section IX). Gel permeation chromatography was used to monitor the molecular weight distribution of resins prepared in both control and radiochemical synthesis runs.

IV. FABRICATION OF RESIN-GRAPHITE TEST COUPONS

The purpose of work in this section was to fabricate test coupons simulating bipolar plates for use in evaluating the corrosion resistance of the various resin-graphite formulations. If corrosion could be controlled by relatively simple means, then possible poisoning from resin degradation products would be much less of a problem. For this reason, work with the goal of improving corrosion resistance was given the most attention. For these studies, 1"x3"x 1/8" composite (75% graphite/25% resin) test coupons were prepared using the two step curing/molding techniques developed in the previous Ashland contract [7] (See Appendix I-A for detailed procedure). Techniques used for fabrication of C-14 containing test coupons were identical to those used for non-labelled coupons.

V. 190°C CORROSION STUDIES WITH TEST COUPONS

Test coupons prepared as described in the preceding section and Appendix I-A were corrosion tested by immersion in 190°C H_3PO_4, contained in Teflon cups, for extended periods of time (up to 2000 hours). Samples of the acid were taken periodically and the amount of resin in solution was determined by radiochemical methods.

From these measurements the amount of resin etched from the coupon was determined. For complete details of this experimental procedure, see sections B and C of Appendix I. Initial corrosion tests were attempted in glass containers; however, the acid was found to attack the glass at this temperature. A precipitate was found in the acid, and in some cases deposited on the coupons. This material was shown by X-ray diffraction to be $Si(HPO_4)2 \cdot H_2O$, with some amorphous silica phosphate. The presence of this material was very deleterious to the test. The use of Teflon containers eliminated this problem and was essential for good results.

The results for several coupons from the initial tests are shown in Figure I. First, it was apparent that some coupons exhibited very good corrosion resistance (less than 0.2% weight loss of the resin) while others, supposedly molded under identical conditions, showed poor corrosion resistance (more than 5% weight loss). In Appendices II and III, detailed results are presented for all coupons tested. Physical examination of the coupons after corrosion tests showed that the more corroded coupons had swelled considerably (up to about 17% increase in thickness). Photographs of a highly etched coupon and one only slightly attacked are shown in Figure 2.

A second, but very important observation from Figure I is that all corrosion takes place in about 300 hours (no matter what the amount of total etching). The mechanism for this passivation is not known. It may be that H_3PO_4 attacks only low molecular weight resin, as well as that not fully crosslinked. Apparently the etching ceases when low molecular weight resin materials are depleted, and probably only fully crosslinked material remains in the coupon.

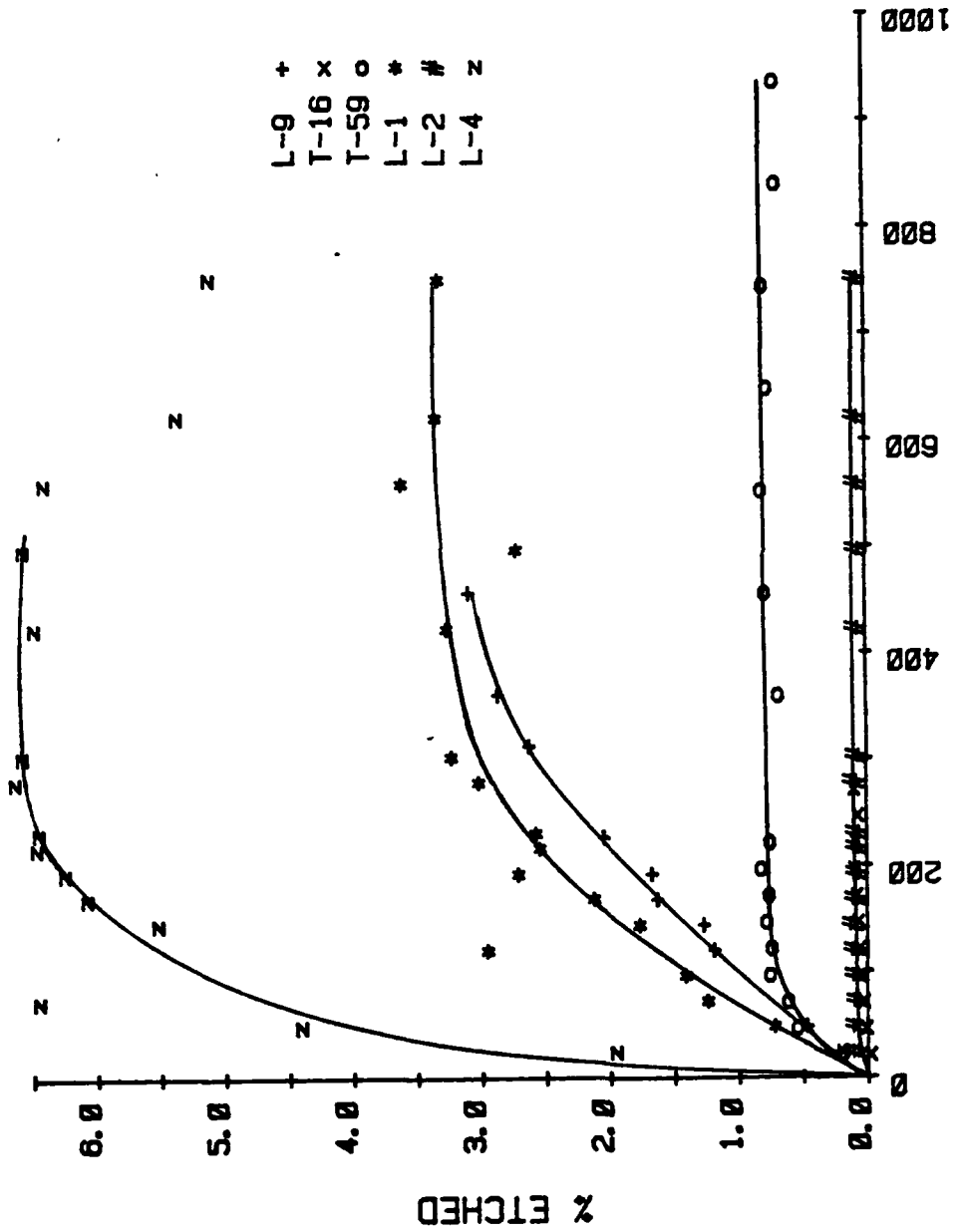


FIGURE 1. Results from initial corrosion tests

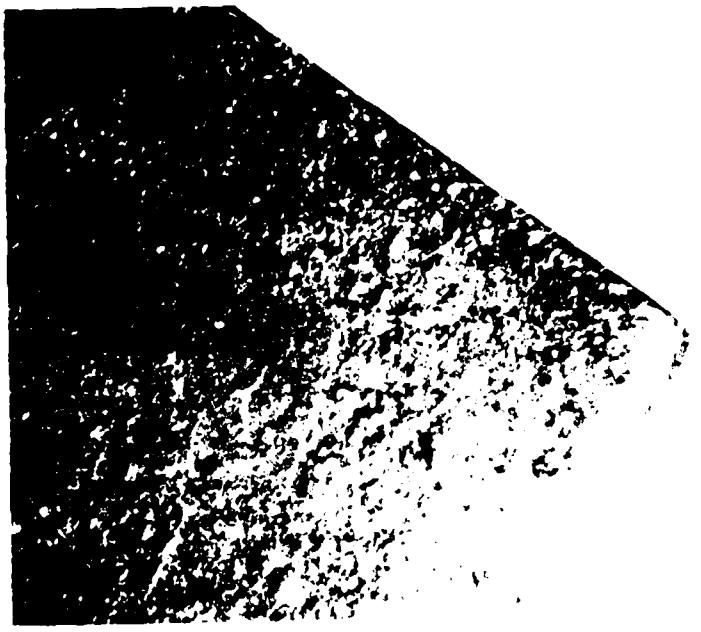


Figure 2a. Coupon M-27, highly etched (notice pits).

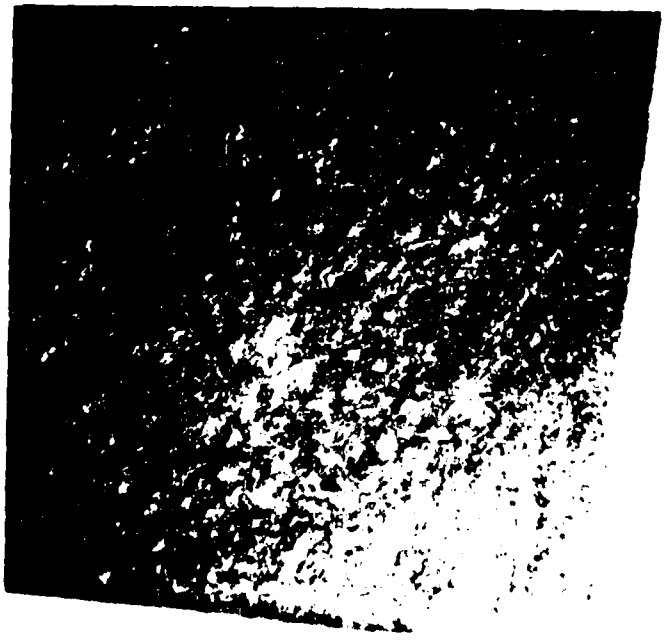


Figure 2b. Coupon M-12, slightly attacked.

All this aside, it is important to note that corrosion takes place only during the first 300 hours.

VI. PREPARATION OF NON-LABELLED DEGRADATION PRODUCT EXTRACTS FOR FT. BELVOIR

The Electrochemical Laboratory at Ft. Belvoir requested that non-radiochemical H_3PO_4 extracts of degradation products from 3 phenolic resins (Arofene 877LF and A-33, and Colloid 8440) be supplied to them to investigate whether "spiking" of operating fuel cells with these extracts would lead to electrode poisoning. Such extracts were prepared via 190°C H_3PO_4 etching of test coupons. In several cases the coupons were crushed before etching to increase surface area. The previously discussed phenomenon of test coupon swelling when H_3PO_4 corrosion rates were large was accentuated greatly with crushed (less than 30 mesh size) coupons.

VII. IMPROVED MOLDING CONDITIONS FOR FURTHER ENHANCEMENT OF COUPON CORROSION RESISTANCE

The previously discussed scattered results from supposedly identical coupons indicated that not all molding and curing processes were under control. Coupon fabrication did not give consistent results, but indications were that under more optimum conditions the resin-graphite coupons should be very resistant to attack by H_3PO_4. As discussed in Section V, one logical area for investigation was more efficient curing (crosslinking of the resin). Other areas for study would be improved resin flow and attempted removal of impurities from the resin.

Molding techniques were varied to increase flow during curing, but to no avail.

Vacuum curing, an attempt to remove impurities prior to corrosion tests, resulted in some improvement in corrosion resistance. However, the corrosion of some coupons was unacceptably high, > 2.5% in two cases (See Table III). Hence, it was necessary to investigate other methods to reduce corrosion.

In order to eliminate the costly and time consuming step of radiolabelled resin synthesis, an alternate procedure was developed to determine the resin concentration in the acid. Also, there were some minor problems with the radiochemical measurements. The activity should monotonically increase or remain constant with time,but it is obvious from the data in Appendix III that this is not always the case. It had been observed that the color of the acid samples corresponded well with the concentration of resin in the acid. Therefore, optical (visible) spectrometry was studied as a potential method for measuring the concentration of resin in the acid. The procedure which was developed is detailed in Appendix I-F. The optical spectrometry method was calibrated using the samples from the tests with radiolabelled coupons. Figure 3 shows the correspondence between optical spectrometric absorption and radiochemically determined concentration. The agreement is good and allowed the use of commercially available resins in corrosion studies . An advantage of visible spectrometry over the radiotracer method is that visible spectrometry takes advantage of the color quenching which plagues the radiochemical method. However, the spectrometric technique is less specific as to where the corrosion products originated than is the radiotracer method.

TABLE III

COUPON	BINDER	MOLDING	% FA**	% ETCHED
L-9	C^{14} A-33 (3717-45)	Standard	0	3.08
L-10	C^{14} A-33 (3717-45)	Standard	0	3.42
M-1	Commercial 877	Hold 220°C, Outgas	0	12.71
*M-2	Commercial 877	Outgas, Hold 220°C	0	2.65
M-3	Commercial 877	Standard	1	3.45
M-4	Commercial 877	Standard	1	1.22
*M-5	Commercial 877	Standard	0	3.35
M-8	Commercial 877	Standard	0	4.95
M-9	Commercial 877	Outgas, Hold 220°C	0	3.42
M-10	Commercial 877	Standard	0	12.30
M-11+	Commercial A-33	Standard	1.5	4.06
*M-18	Arofene 555 (Steam Stripped)	Standard	0	0.43

TABLE IV

*M-12	Commercial A-33	Standard	1.5	0.29
*M-13	Commercial A-33	Standard	1.5	0.72
*M-14	Commercial 877	Standard	1.5	0.20
*M-15	Commercial 877	Standard	1.5	0.21
*M-16	C^{14} A-33 (3717-45)	Standard	1.5	0.15
*M-17	C^{14} A-33 (3717-45)	Standard	1.5	0.27

+ All coupons contain 6% hexamethylenetetramine ("hexa") except M-11 which contained 11.5%

* Indicates coupons post-cured in vacuum. All others were post-cured in air at 220°C.

** FA - Chemical (flow) additive

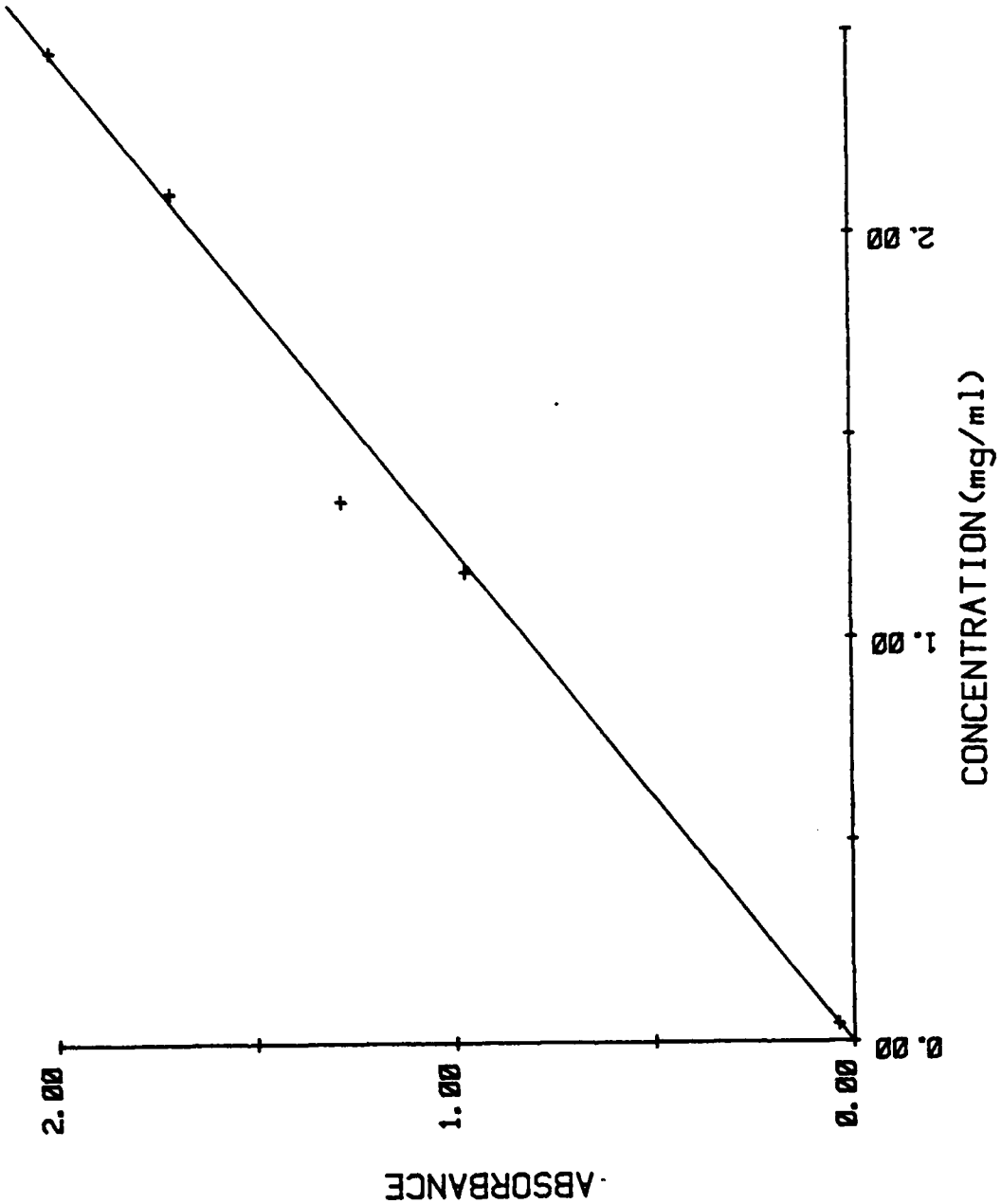


FIGURE 3. Absorbance at 590 nm versus concentration determined from radiochemical measurements.

Salicylic acid is used as a curing aid in some commercial resin formulations. The use of this additive was evaluated in this study, but the results were unfavorable (see Appendices II and III). In fact, higher corrosion rates for test coupons were observed with salicylic acid than without.

As this program progressed, it became apparent that an improvement in resin flow properties during molding (in the early stages of cure where the cross-linking degree is low) was very desirable. Resin flow is usually enhanced when the free phenol content of the resin is low. This was found to be true in this study, as is shown by the results in Table III. The coupon, M-18, prepared from low phenol resin (Arofene 555) showed good corrosion resistance, as can be seen also from the data in Appendices II and III.

The use of a chemical additive to improve resin flow during molding was another approach investigated. Initial results indicated much lower corrosion of test coupons in 190°C H_3PO_4. To check reproducibility, several additional coupons containing this flow enhancing additive were tested, and results were very favorable as shown in Figure 4. Fairly consistent, low (< 0.3% weight loss) * results were obtained in most cases. The earlier problems of higher corrosion rates and inconsistent results thus appeared to have been due to insufficient resin flow in the mold before crosslinking becomes the dominant factor. Use of resin formulations with slower cure rate properties and an additive for improved resin flow appear to be the keys to enhanced corrosion resistance for bipolar plates.

The mechanism for passivation is unknown, but as noted before essentially all

---

* See Table IV and Appendix II

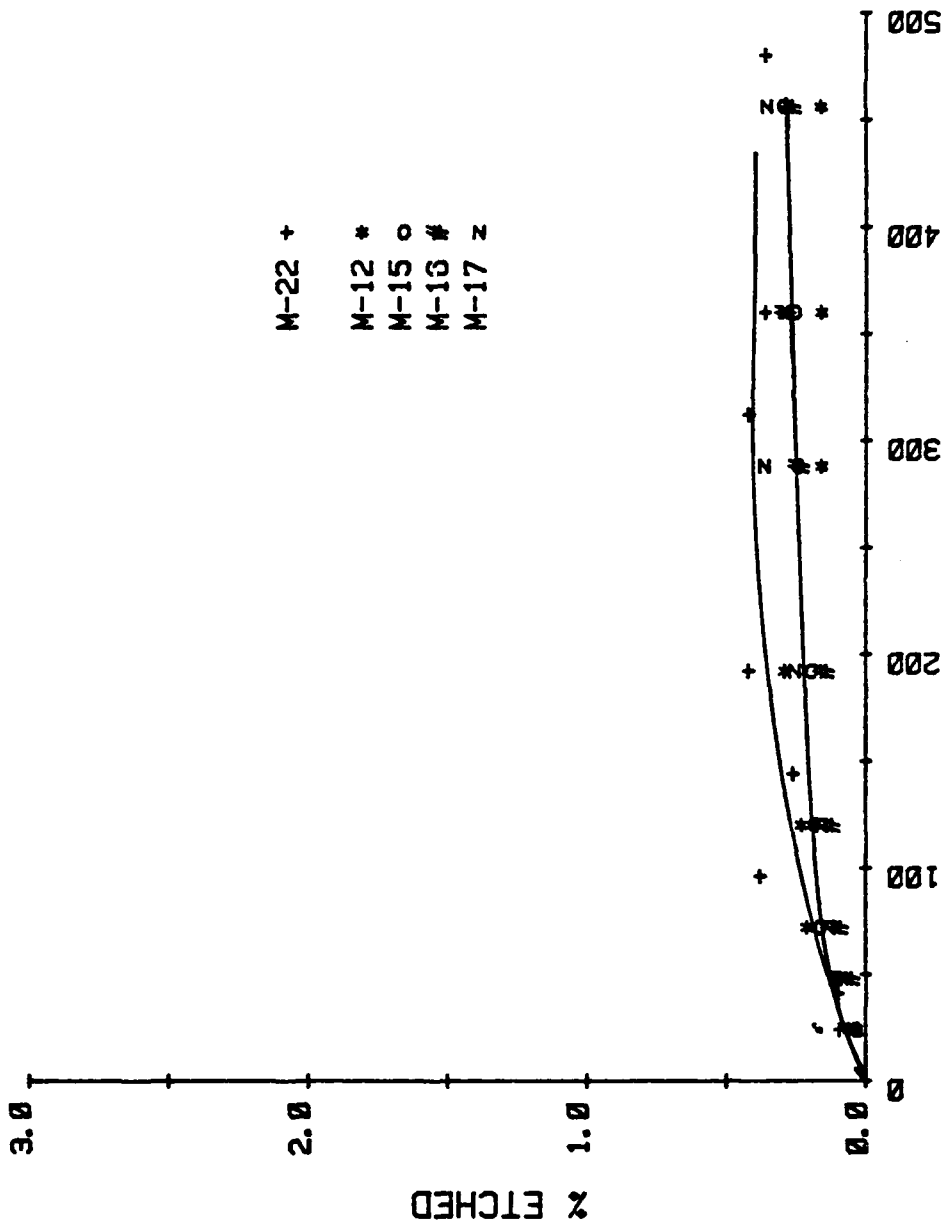


FIGURE 4. Test results from coupons with chemical additives.

corrosion takes place in the first 300 hours*. This was also observed in a test where the acid was changed for each sampling (see Figure 5). Therefore, pre-etching the bipolar plate acid reservoir with H_3PO_4 could be beneficial. However, pre-etching with an organic solvent, acetone (note-coupon M-30, Appendix II), was extremely deleterious. The coupon severely cracked and corrosion was very pronounced.

VIII. INVESTIGATION OF POSSIBLE BLOCKING/POISONING OF Pt ELECTRO-CATALYST BY RESIN DEGRADATION PRODUCTS

Some uncertainty still exists concerning whether or not the Pt electro-catalyst is poisoned by phenolic resin degradation products from hot H_3PO_4 attack on the bipolar plates. A test of possible poisoning or blocking of the Pt/carbon electro-catalyst was considered necessary in this program. The plan was to expose fresh electro-catalyst particles ** to a C-14 containing extract of resin degradation products obtained through prolonged 190°C H_3PO_4 etching of test coupons.

Initial studies here with Matthey-Bishop Pt/carbon electro-catalyst and the corresponding carbon black support established that appreciable quantities of radioactivity adsorbed on the carbon black support alone. A catalyst sheet *** treated with radiolabelled extract was washed with H_2O and dried. It was

* Examination of the corrosion versus time data in Appendix III indicates that the % etched at 100 hours is a fairly good indicator to distinguish an ultimately good coupon from a bad one. Coupon M-25 seems to be the only anomaly, and it contained two additives which were competitive, one helpful and the other deleterious. Therefore, screening tests for corrosion resistance could be run for shorter times than those used here, in most cases.

** 10% Pt on heat-treated carbon black support (Matthey Bishop No. TS-1345).

*** Pt/C granules with polytetrafluoroethylene binder (25%) supported on porous graphite paper.

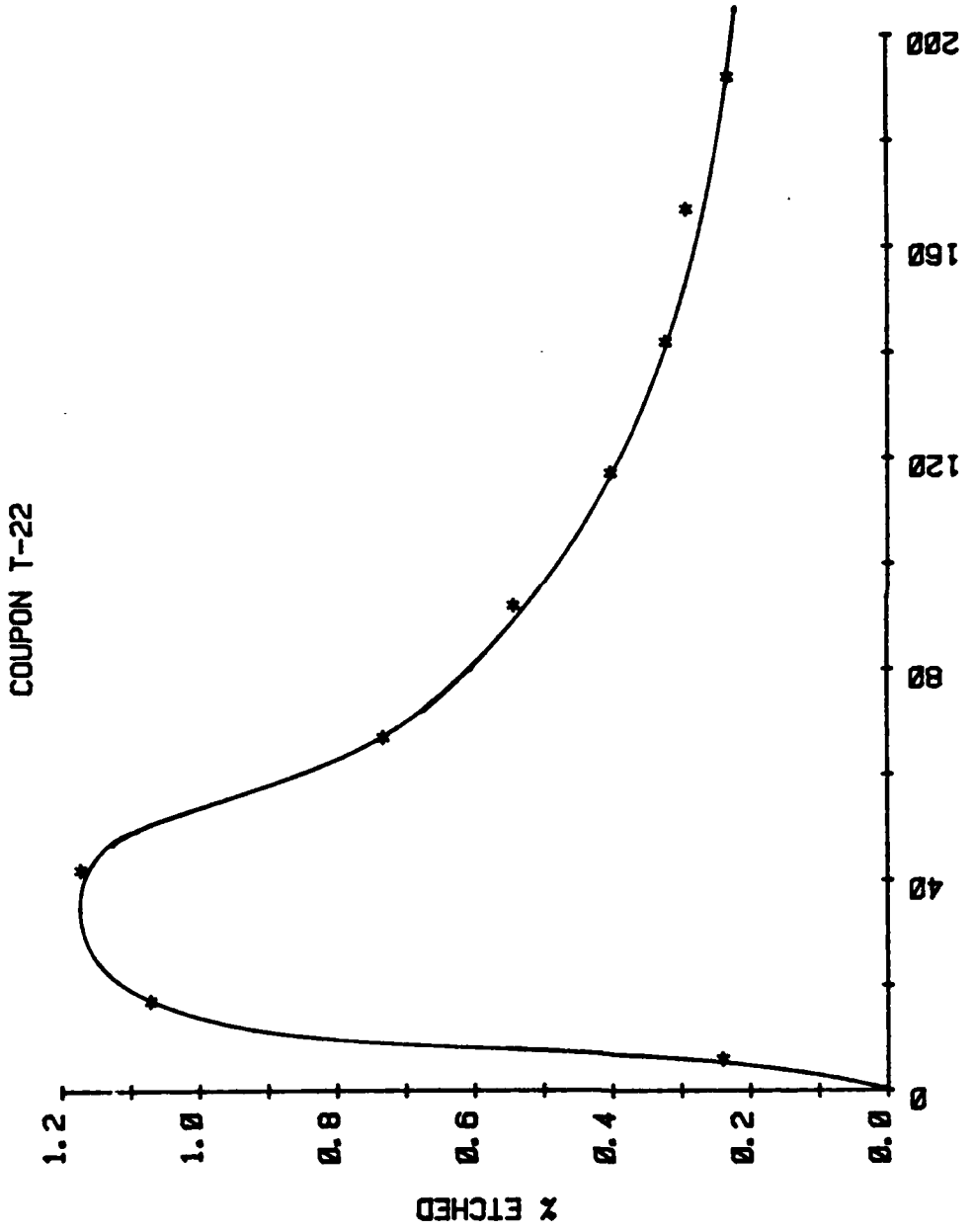


FIGURE 5. Corrosion versus time for coupon where the acid was changed after each sample was taken.

then combusted in a scintillation vial and the adsorbed activity counted. The test showed that 342 μg/(g catalyst sheet) or 0.7 μg/cm^2 of catalyst sheet was adsorbed. Consequently, prospects were not considered good for development of a procedure which could measure differences between C-14 adsorbed upon the Pt/carbon catalyst and upon the support alone.

An alternate method was considered essential for investigating the question of poisoning or blocking of the Pt crystallites alone by resin degradation products. Carbon monoxide chemisorption has been used rather extensively for measuring the "active" surface area of Pt on several support types [8,9,10]. Some uncertainty did exist concerning whether the hydrogen deficient nature of the carbon black support might cause reproducibility problems with measurements on the fuel cell Pt electro-catalyst. Pre-treatment of fresh and used electro-catalyst with hydrogen was considered a possible remedy.

Two methods were used here to measure the active surface area of Pt crystallites before and after prolonged adsorption of resin degradation products from an extract. Both techniques involved a H_2 pre-treatment and B.E.T. - type surface area measurements involving injection of CO doses into a carrier gas passing over the catalyst. The two methods employed (see Appendix I-G for detailed procedures) differed in the carrier gas employed and in the resultant gas measured by the detector. The first procedure, denoted as the H_2 displacement method, was developed by Dr. James Palmer [11] (Ashland Oil--Refinery R&D Lab) and employed 5% H_2 in nitrogen as the carrier. The second method--denoted as the CO chemisorption difference technique--was developed by Dr. Ralph Dalla Betta [12] (now at Catalytica Associates) and used pure hydrogen as the carrier. In the H_2 displacement method, peak area measurements are made on H_2 displaced from the Pt surface when CO is injected. In the second

procedure a CO dose is injected into the H_2 carrier gas and measurement is made of the CO(area) not chemisorbed onto the sample and compared to CO (area) from the same volume of CO injected thru a bypass loop. Even though absolute values of the Pt surface areas measured by each method may not agree, each was self-consistent. The relative values are meaningful; that is, Pt surface areas after treatments should be compared to the area of the fresh catalyst. A summary of CO chemisorption results is given in Table V.

The results presented in this table unfortunately are not as conclusive as was hoped for. The hydrogen displacement method indicated little or no poisoning or blocking of active Pt surface area on the particulate catalyst. The CO chemisorption difference method indicated that active Pt surface area was decreased by exposure to high purity H_3PO_4, and was further decreased by exposure to the H_3PO_4 extract of resin degradation products; however, total blocking or poisoning of the Pt was not shown by the CO chemisorption difference method on any of the numerous individual samples measured.

Thus at present no explanation can be offered for the difference in active Pt surface areas obtained with the two methods. Discussions have been held with the developers of both methods, but no conclusions were reached.*

* However, if it is assumed that Pt surface area results on resin-exposed catalyst by the H_2 displacement method are "high", and that--in reality some poisoning/blocking of Pt has actually occurred--then it has to be assumed that resin-exposed catalysts somehow adsorb more H_2 than fresh catalyst in the pre-treatment step.

TABLE V

"Active" Pt Surface Areas (Average) for Electro-Catalyst Particles Before and After Exposure to H_3PO_4 and Resin Degradation Product Extracts in H_3PO_4

Sample	Average Active Pt Surface Area (m^2/gram of catalyst)		
	By CO Chemisorption Difference Method	By H_2 Displacement Method (Performed Here)	By H_2 Displacement Method (Performed at Ashland Refinery)
Fresh Pt (10% w) on Carbon Black (Mfg's quoted surface area value=14.6 m^2/gm)	7.5	7.6	14.6
After Exposure to High Purity H_3PO_4	3.5	6.0	--
After Exposure to Extract of Resin Degradation Products	1.3	5.5	14.6

Mechanical blocking* is a possible explanation for the inconclusive results obtained, but in no case was total blocking or poisoning of the electro-catalyst observed. However, more definitive, positive information was obtained from C-14 radiotracer measurements in connection with extended fuel cell operation, as discussed in the next section.

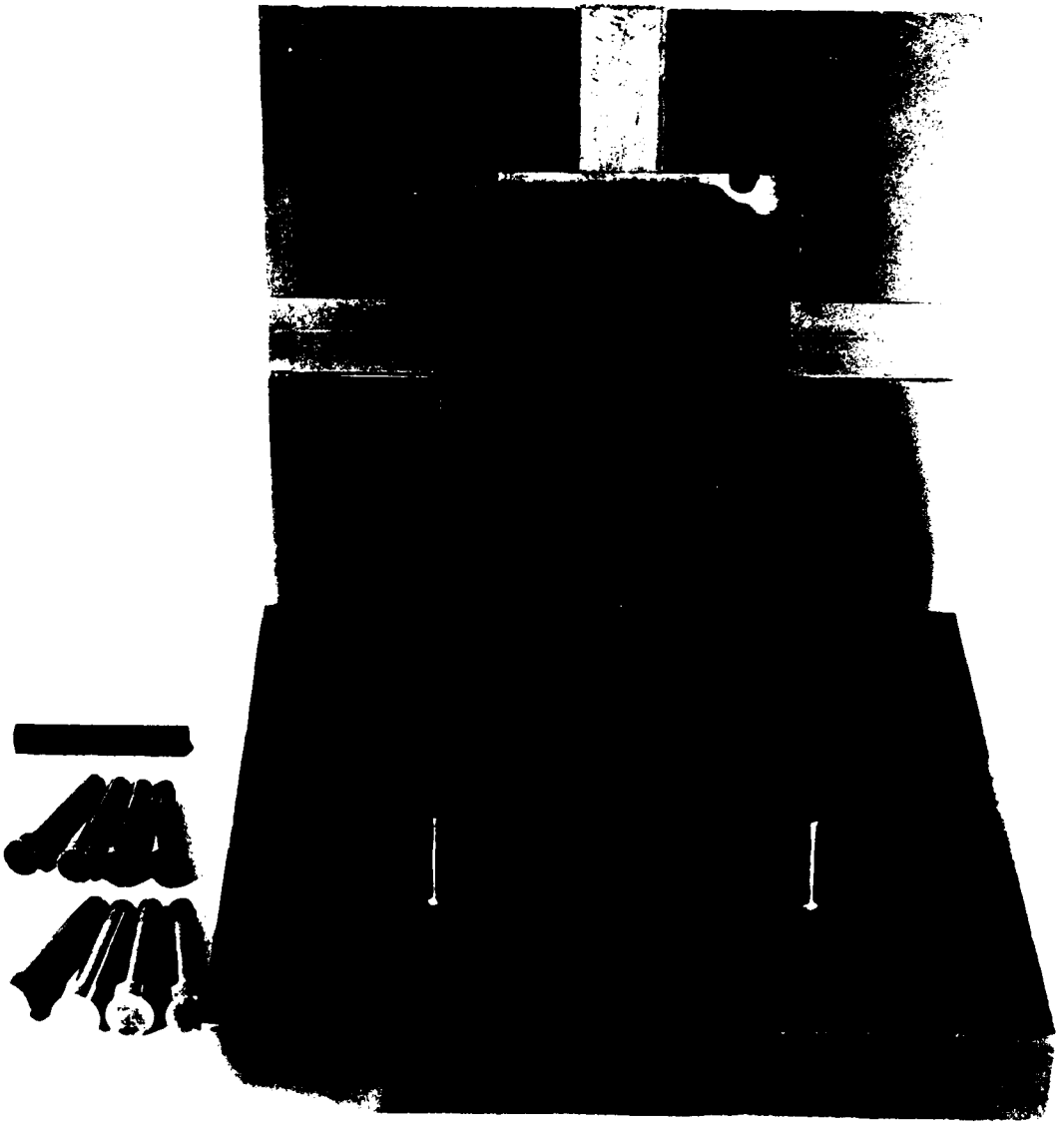
IX. FUEL CELL OPERATION WITH C-14 LABELLED BIPOLAR PLATES

Since peroxides are formed in an operating fuel cell, the corrosion of the phenolic resin under operational conditions could be different from that under static etching conditions. Therefore, it was necessary to monitor corrosion and to investigate poisoning in operating fuel cells. The approach involved fabrication of bipolar plates from C-14 radiolabelled resins. In this study, only the reservoir area of the plate was labelled since that is the only area on the plate which comes in contact with hot H_3PO_4. If poisoning should occur, then radioactivity from the resin or its degradation products should be found on the catalytic electrode sheets; however, the converse is not true. Presence of radioactivity on the electrodes does not necessarily mean poisoning has occurred. In addition, Pt surface areas on catalyst sheets were also measured by the H_2 displacement technique (see previous section).

To accomplish the above goals, a mold for producing bipolar plates had to be designed and fabricated. Figure 6 shows a photograph of the mold. With this mold, bipolar plates for 2" x 2" (electrode area) miniature fuel cells

---

* It should be mentioned that considerable trouble was encountered in removing precipitated resin products from the electro-catalyst particles after exposure to the degradation products extract. A pre-washing of exposed particles in glacial H_3PO_4 was essential, before washing/centrifugation with H_2O, to prevent a heavy precipitation of resin products on the particle.



could be prepared. Bipolar plates from both Arofene A-33 and 877LF resins were molded and used in this program.

The first operational fuel cell (containing an 877LF bipolar plate) was brought up by setting the gas flows (60 cc/min air and 40 cc/min H_2) and then raising the temperature to 190°C. It was operated open circuit for 110 hours to determine its stability and operating characteristics. Then a resistive load was added. The cell operated for about 180 hours with an output of about 0.65 V. and 0.65 A. The operating temperature varied from 160°C to 195°C. Catastrophic failure occured at the 180 hour point. Post-test examination indicated a failure of the acid wick.*

Two other miniature fuel cells were next placed into operation, using bipolar plates with labelled A-33 resin in the reservoir area. Gas flows were the same as above. The operating temperatures were 160°C for cell number 2 and 190°C for cell number 3. In Table VI are given the operational parameters for the three fuel cells. The last two cells operated for about 1300 hours before being disassembled. The anode sheet in cell 3 was partially stuck to the wick, but most of it could be removed. The sheets were then stripped from the backing paper, washed, and dried (for complete details see Appendices I-D and I-G). Surface areas were measured by the H_2 displacement method and C-14 radioactivity was measured on each sheet (see Appendix I-D for details). The results of these tests are listed in Table VII.

---

* A paper-like matrix prepared from blown phenolic fibers and a phenolic resin dispersion.

TABLE VI

Fuel Cell Number	Resin Type	Open Circuit Voltage	Load Volts	Load Amps	Temperature °C	Remarks
1	877LF	0.88	0.65	0.65	160-195	Wick failure at 180 hours
2	A-33	0.97	0.65	0.55	160	Still operational after 1300 hours
3	A-33	1.03	0.70	0.70	190	Still operational after 1344 hours

TABLE VII

Pt/Carbon Electrode Sheet	Surface Area (m^2/gm*)	Radioactivity
Fresh (unused)	13.3	0
Used, Cell 2	5.1	0 (anode) 0 (cathode)
Used, Cell 3	2.9	0 (anode) $\approx$0 (cathode) **
Acid Treated	6.8	
Extract Treated	10.7	

* Per gram of Pt/carbon catalyst, assuming 25% Teflon in the catalyst sheet.

** Extremely minute traces detected ($\sim$ twice background).

The above measurements indicate that there was no adsorption of C-14 labelled resin degradation products on the electrodes. These results, therefore, indicate that resin degradation products could not have been a poison. The observed loss of Pt active surface area must then be due to another mechanism. Two possible candidates are Pt crystallite sintering and loss of Pt particles from the electrode due to erosion of the carbon support (thus undercutting the Pt crystallites). A recent paper[3] by investigators elsewhere discusses the use of transmission electron microscopy for investigating Pt crystallite sintering. The erosion of the carbon support is still under study in other laboratories.

Physical inspection of the plates from all three cells showed that there was no apparent H_3PO_4 etching of the resin. Indeed, acid samples from cells 2 and 3 were dispersed into a scintillation counting solution, and measurements of the activity made. No radiochemical activity was found, as was also the case with the electrodes.

X. CONCLUSIONS

Arofene A-33 and 877LF -- when molded and cured using the improved techniques developed under this contract -- are promising candidates for use in preparing composite (graphite powder/phenolic resin) bipolar plates which are highly resistant to corrosion by 190°C H_3PO_4. These conclusions are based on (1) the low etching results obtained with A-33 and 877LF test coupons in 190°C H_3PO_4, and (2) the results (no C-14 adsorption found on electrodes) with the two operating fuel cells containing A-33 bipolar plates. These results suggest that a hot H_3PO_4 pretreatment of the bipolar plate reservoir area could result in little or no etching by H_3PO_4 in subsequent fuel cell operations.

The main features of the modified curing/molding procedure developed (but not fully optimized) here for bipolar plate fabrication are the use of a chemical additive and techniques to improve resin flow properties during cure, and the employment of an extended (20 hour) vacuum oven post-cure of the plates.

The results obtained with the modified formulation and curing techniques suggest that, with improved resin flow during molding, it may be possible to lower the bipolar plate resin content below 25% (the amount used in this study). This could result in greater electrical conductivity for the bipolar plate, without introducing increased plate porosity (which would lead to increased H_2 permeability and greater susceptibility to H_3PO_4 attack). This would require careful verification.

Steam stripping of the phenolic resin to remove excess phenol and reaction by-products may be a useful technique for improving test coupon resistance

to hot H_3PO_4. This approach is suggested by the limited results obtained here, but considerably more work is needed for verification.

No definite conclusions can be drawn from the work using either of the two CO-type techniques to monitor poisoning or blocking of the supported Pt electro-catalyst by resin degradation products (adsorbed from H_3PO_4 extracts). More work would be required to rationalize the high (no blockage) Pt surface area results obtained using the H_2 displacement method with the lower surface area results obtained using the CO chemisorption difference method. It is important to note again that in no individual measurement case was complete blockage of the Pt surface observed.

A different, known mechanism for loss of Pt active surface area in fuel cell electro-catalysts is sintering of the Pt particles[3] alone or in conjunction with the erosion of the carbon black support, as was discussed in the preceding section.

XI. GENERAL RECOMMENDATIONS

Based on the results obtained during this contract, our principal recommendation would be that further, more extensive bipolar plate developmental work be undertaken with Arofene A-33 and 877LF resins to optimize the improved formulation and curing techniques developed in this study. After establishment of an optimized formulation/curing method, bipolar plates prepared by this procedure would have to be extensively tested via monitoring the performance parameters of a sizeable number of miniature fuel cells, using the usual Ft. Belvoir electrochemical test procedures (or their equivalent).

Although our results indicate that hot H_3PO_4 pretreated bipolar plate reservoirs should exhibit essentially no subsequent corrosion, different etching mechanisms (e.g. peroxide attack) could be encountered in operating fuel cells. Certainly, carbon-14 radiotracer techniques could be used to advantage in further developmental work to investigate the etching mec anism question in operating miniature fuel cells. For example, periodic monitoring of small H_3PO_4 aliquots removed from the bipolar plate reservoir should establish whether or not plate "static" pretreatment with hot H_3PO_4 is sufficient to eliminate subsequent etching in an operating fuel cell. This C-14 approach at the same time would allow monitoring to determine if C-14 chemisorption occurs on electrodes during operating periods greater than those in the present study (or when a bipolar plate molded under conditions known to lead to etching is used in a fuel cell).

Further work on the steam stripping of raw resins to remove potentially etchable by-products is worthy of consideration.

The possibility exists that other phenolic resins could be developed even more resistant to hot phosphoric acid than the two resins in this study. New candidate resin structures could be screened more rapidly using the visible spectrometric procedure developed in this study. Radiochemical resin synthesis and testing work could be deferred until very promising resin candidates are found.

REFERENCES

1. S.G. Abens, B.S. Baker, and I. Michalko, "Fuel Cell Stacks", Final Technical Report on Contract No. DAAK02-74-C-0367, June, 1977; Sponsored by U.S. Army Mobility Equipment R&D Command, Ft. Belvoir Virginia.

2. A. Kaufman, "Phosphoric Acid Fuel Cell Stack and System Development", Technical Progress Report for Quarter Ending Sept. 30, 1979, Contract No. DE-AC-03-78-ET 15366; Sponsored by U.S. Dept. of Energy, Administered by NASA Lewis Research Center.

3. G.A. Gruver, R.F. Pascoe, H.R. Kunz, "Surface Area Loss of Platinum Supported on Carbon in Phosphoric Acid Electrolyte", J. Electrochem. Soc. 127, 1219 (1980).

4. P. Stonehart, J. MacDonald, V. Jalon and J. Baris,"Development of Electro-Catalysts and Conductive Substrates for Phosphoric Acid Cathode", pp. 102-105, Long abstract of paper presented to National Fuel Cell Seminar, Bethesda, Maryland, June 26-28, 1979.

5. L.G. Christner, "Technology Development for Phosphoric Acid Fuel Cell Powerplant (Phase II)", 3rd Quarterly Report for Contract No. DEN 3-67, June, 1979. Sponsored by U.S. Dept. of Energy; Administered by NASA Lewis Research Center (DOE/NASA/0067-79-2), NASA Report No. CR-159705.

6. H.C. Maru, L. G. Christner, S.G. Abens, and B.S. Baker,"Phosphoric Acid Fuel Cell Stack and Technology Programs", pp. 86-90, Long abstract of paper presented to National Fuel Cell Seminar, Bethesda, Maryland, June 26-28, 1979.

7. P.M. Colling, J.E. Martin, and R.V. Norton, "Selection and Evaluation of Carbon-Resin Composites for Bipolar Plates for Hydrogen Fuel Cells", Final Technical Report for Contract No. DAAK70-77-C-0151, Completed Sept.1978, Sponsored by U.S. Army Mobility Equipment R&D Command, Ft. Belvoir, Virginia

8. J. Bett, K. Kinoshita, K. Routsis,and P. Stonehart,"A Comparison of Gas-Phase and Electrochemical Measurements for Chemisorbed Carbon Monoxide and Hydrogen on Platinum Crystallites", J. Catal. 29, 160 (1973).

9. T.A. Dörling and R.L. Moss, "The Structure and Activity of Supported Metal Catalysts, II. Crystallite Size and CO Chemisorption on Platinum/Silica Catalysts". J. Catal. 7, 378 (1967).

10. J.E. Benson and M. Boudart, "Hydrogen-Oxygen Titration Method for the Measurement of Supported Platinum Surface Areas", J. Catal. 4, 704 (1965).

11. J. Palmer, Private Communication.

12. R.A. Dalla Betta, Private Communication

ACKNOWLEDGMENTS

The authors wish to express their gratitude to several persons whose assistance contributed greatly to the success of this project: Corbett L. Taylor, for performing the majority of the experimental work, particularly in the radiochemical analysis and resin curing areas; G. Fred Watts, for his expert counseling services in phenolic resins chemistry area; Alan H. Boyer, who carried out most of the syntheses of radio-labelled resins; and Richard V. Norton and John E. Martin who provided important counsel concerning experimental techniques developed during their previous related fuel cell contract.

APPENDIX I

EXPERIMENTAL PROCEDURES

A. Molding Coupons and Bipolar Plates

The fabrication of the coupons was the same as given in reference 7, and was basically a kiss and press technique. This had not been optimized and some additional work would be required to do so. The conditions were as follows: The Arofene resin was ground and sized to < 200 mesh. It was then mixed with hexamethylenetetramine (hexa). This mixture was then blended with Asbury graphite Filler A (50% 7101, 40% 4015, and 10% micro-250) such that 75% was graphite and 25% resin/hexa. Chemical additives can be added at any stage of this process. For forming, the mold was heated to 65.5°C and then the graphite/resin mix was charged. The mix was pressed to 2X final thickness while heating the mold to 104.4°C. At this point the pressure was released and the ram removed to allow gases to escape. The ram was replaced and the mold was heated to 185°C. It was then pressed to final thickness by applying approximately 5300 psi (3200 psi for the plates) and holding at temperature and pressure for 20 minutes. After this time the pressure was released and the molded piece was removed.

After the composite cooled, it was placed in an oven at 220°C for 20 hours for post-curing. A vacuum ($\sim 10^{-1}$ torr) was applied during this time for some coupons and bipolar plates.

B. Corrosion Tests

A coupon (molded as in Appendix I-A) was broken in half, and a 1/8" diameter hole was drilled in each half to allow suspension from the lid of a 100 ml Teflon container by means of a Teflon string. A 1/4" Teflon spacer was used to keep the halves separated during the test. The coupon was then placed in the Teflon cup containing 93.5 ml of Baker's H_3PO_4 (85.6%). The assembly was placed in an oven at 200°C. At various intervals 0.3 ml of acid was removed for radiochemical counting or spectrometric measurements, and was replenished by 0.3 ml of fresh preheated (200°C) acid. At the end of the prolonged corrosion test the acid was saved to be used in fuel cell poisoning studies.

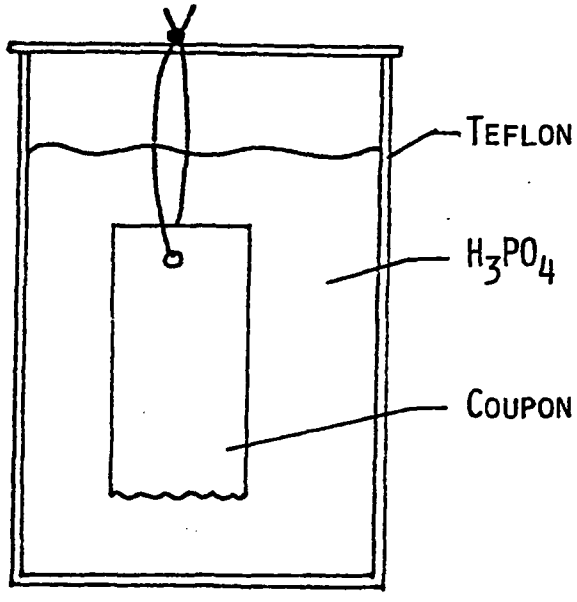
C. Counting Procedures for Corrosion Tests

The 0.3 ml acid sample was diluted 9 to 1 with H_2O. Then 1 ml of diluted etching product was placed in 10 ml of dioxane scintillation cocktail (for more concentrated samples, less of the diluted acid was used to reduce color quenching). The dioxane solutions were counted in a Beckman LS-100 liquid scintillation counter. A spiking procedure was used to determine the counting efficiency. This procedure required 50 μ l of C^{14} radiochemical standard (New England Nuclear lot no. 697-242, containing 4.5×10^5 dpm/ml activity) in each acidic-sample cocktail solution. The spiked solutions were counted and comparisons with raw counts allowed the counting efficiency to be calculated.

D. Counting Procedures for Catalyst Sheets

The catalyst sheets were separated from the backing paper. A small (approximately 1/16 in^2) sample was taken and placed in a glass liquid scintillation vial with a cap containing a hole fitted with a silicone

FIGURE 7. Schematic of a corrosion test.



rubber septum. The vial was flushed with O_2 and immediately capped. Then 10 ml of O_2 was injected into the vial with a hypodermic needle through the septum. The sheet was combusted using an infrared lamp for ignition. The vial was cooled to room temperature and 10 ml of cocktail (180 ml ethanol-amine, 290 ml 2-methoxy ethanol, 530 ml toluene, and 5 gm PPO) was injected. The solution was counted in the Beckman LS-100 Counter, and the spiking technique was used for calibration. For background counts a fresh catalyst sheet was used.

E. Counting Procedure for Insoluble, Non-Combustible Powders

The carbon black support and Pt powder were each treated with the H_3PO_4 extract from corrosion tests on coupons containing a radiolabelled resin. Each powder was filtered, then washed with H_3PO_4 and H_2O using a vacuum filter funnel, and finally dried under vacuum at 150°C. Samples were placed into glass scintillation vials along with 3 glass beads (1/8" diameter). The vials were shaken on a vibrating ball mill for 5 minutes to powder the samples since they coagulate during the treatment. The glass beads were removed and the vial was filled approximately 75% full with Cab-O-Sil to act as a gelling agent. Then 10 ml of dioxane counting cocktail was added and shaken for 2 minutes to mix the materials. The material was then counted, and the spiking technique was used for calibration.

F. Visible Optical Spectrometry

The 0.3 ml samples from the corrosion tests were diluted with 9.7 ml of fresh H_3PO_4 (Baker's 86.5%). A portion of the diluted sample was put in a cuvette and then placed in a Bausch and Lomb spectrometer tuned to 590 nm. This wavelength had previously been determined to be the optimum

wavelength. Fresh acid was used as a blank for zeroing the instrument. The absorbance of sample was then measured. For calibration, the absorbances were measured on samples of known concentrations. These concentrations were determined from C^{14} radiochemical measurements of corrosion extracts.

G. Surface Area Measurements

To determine possible catalyst poisoning, first approximately 0.5 g of powder (Pt/carbon, colloidal Pt , or carbon black) was placed in a 10 ml Teflon beaker and covered with acid extract (or pure acid for blanks). The contents were mixed to ensure complete wetting, then placed in an oven at 190°C for either 24 or 48 hours. The material was cooled, transferred to a centrifuge tube, and fresh acid added to give a volume of about 30 ml. These tubes were shaken to disperse and suspend the powder. This suspension was then centrifuged and the acid decanted. Three washes with acid followed by at least 5 washes with H_2O were done to remove nonadsorbed resin extract. The material was then dried at 150°C under vacuum; usually 48 hours at temperature was required.

Surface areas were measured on the dried extract-treated powders, using a continuous flow, B.E.T.-type apparatus ("Quantasorb");* First the sample was weighed in a cell and then purged in a stream of H_2. While in the H_2 stream, the samples were heated to 150°C and held there for a minimum of 1 hour. Two separate methods were used to determine the surface area. The first method measures the H_2 displaced by CO injection and chemisorption, while the second measures the difference between CO injected thru the sample (and thus partially chemisorbed) and CO injected thru a bypass loop.

* Manufactured by Quantachrome Corp., Syosset, N.Y.

1. H_2 Displacement Method [11]

In this method a flow of 5% H_2/95% N_2 was established through the instrument and sample. Then 0.2 ml CO was injected through the sample. This injection was repeated until a negative peak occurred indicating complete CO breakthrough and no further CO chemisorption. The detector was set to monitor H_2 as a positive deflection. The sensitivity for H_2/CO was approximately 10/1. For calibration the flow was diverted from the sample through a bypass loop and 0.1 ml H_2 was injected. The polarity on the detector was reversed and 0.2 ml CO was injected. The Pt surface area was proportional to the H_2 evolved and no assumptions on the Pt/CO adsorption ratio stoichiometry need to be made.

2. CO Chemisorption Difference Method [12]

A flow of H_2 was established through the Quantasorb instrument and sample. Then 1.0 ml CO was injected through the sample. The flow was diverted to a bypass loop and 1.0 ml CO was injected through the instrument. The difference in these readings was proportional to the Pt surface area and CO/Pt adsorption ratio was assumed to be 1.

H. Resin Post-Cure By-Products Removal by Vacuum

There was concern from the beginning of this project as to whether volatile curing by-products remaining in the bipolar plates could contribute to potential electrode poisoning. Early in the program, vacuum oven post-curing (20 hours at 220°C) was adopted as a standard step to take care of

this problem and to obtain better mechanical strength for the bipolar plates and test coupons.

A brief study was undertaken later to gain some information concerning the volatile materials removed by the vacuum oven post-cure step. A freeze-trap (CO_2-dry ice) procedure was used to collect post-curing volatiles. Cursory NMR, infrared and gas chromatography characterization work was carried out. Phenol accounted for 90% of the organic material, while a second organic component accounted for an additional 6%. About a dozen other trace organic components were also detected.

APPENDIX II

COUPON	BINDER	CHEMICAL ADDITIVE/%	POST CURE	FINAL % ETCHED	REMARKS
T-16	$C^{14}877$	0	Reg.	0.13	
T-22	$C^{14}877$	0	Reg.	5.50	9% hexa
T-59	C^{14}A-33 (3717-45)	0	Reg.	0.75	
T-60	C^{14}A-33 (3717-22)	0	Reg.	0.30	
L-1	C^{14}A-33 (3717-45)	0	Reg.	2.86	
L-2	C^{14}A-33 (3717-45)	0	Vac.	0.10	
L-3	C^{14}A-33 (3717-45)	0	Reg.	3.30	9% hexa
L-4	$C^{14}877$	0	Reg.	5.37	
L-5	$C^{14}877$	0	Reg.	9.10	9% hexa
L-6	C^{14}A-33 (3717-22)	0	Vac.	0.40	
L-7	C^{14}A-33 (3717-22)	0	Reg.	4.80	Prolonged molding
L-8	C^{14}A-33 (3717-22)	0	Reg.	4.25	Prolonged molding, 9% hexa
L-9	C^{14}A-33 (3717-45)	0	Reg.	3.08	
L-10	C^{14}A-33 (3717-45)	0	Reg.	3.42	
M-1	Commercial 877	0	Reg.	12.71	Molding: Held @220° (20 Min)→outgas
M-2	Commercial 877	0	Vac.	2.65	Molding: Outgas→Held @220° (20 Min)
M-3	Commercial 877	FA/1	Reg.	3.45	
M-4	Commercial 877	FA/1	Reg.	1.22	
M-5	Commercial 877	0	Vac.	3.35	
M-8	Commercial 877	0	Reg.	4.95	
M-9	Commercial 877	0	Reg.	3.10	Molding:Outgas → Held @220° (20 Min)
M-10	Commercial 877	0	Reg.	12.30	
M-11	Commercial A-33	FA/1.5	Reg.	6.00	11.5% hexa
M-12	Commercial A-33	FA/1.5	Vac.	0.21	
M-13	Commercial A-33	FA/1.5	Vac.	1.45	
M-14	Commercial 877	FA/1.5	Vac.	0.28	
M-15	Commercial 877	FA/1.5	Vac.	0.33	
M-16	C^{14}A-33 (3717-45)	FA/1.5	Vac.	0.31	
M-17	C^{14}A-33 (3717-45)	FA/1.5	Vac.	0.40	
M-18	Arofene 555	0	Vac.	0.43	Purified resin (by steam)
M-19	Commercial 877	0	Reg.	4.20	
M-20	Commercial 877	0	Vac.	7.10	
M-21	Commercial 877	FA/1.5	Vac.	1.75	
M-22	Commercial 877	FA/1.5	Vac.	0.38	
M-24	Commercial 877	FA/1.5 SA/1	Vac.	0.60	
M-25	Commercial 877	FA/1.5 SA/1	Vac.	10.49	
M-26	Commercial 877	SA/1	Vac.	10.5+	
M-27	Commercial 877	SA/1	Vac.	10.5+	
M-30	Commercial 877		Vac.	10.5+	Extracted with acetone before acid etch

Note: All binders contain 6% hexa unless otherwise noted

All coupons contain 25% Binder, 75% Filler A

Filler A:

50% Asbury 7101

40% Asbury 4015

10% Asbury Micro 250

*FA = flow modifying agent

SA = Salicylic Acid

APPENDIX III

COUPON TIME-HRS.	T-16 % ETCHED	COUPON TIME-HRS.	T-22 %ETCHED	COUPON TIME-HRS.	T-59 % ETCHED	T-60 % ETCHED
21	0.01	6	0.24	21	0.23	0.07
46	0.04	17	1.31	46	0.58	0.11
71	0.06	42	2.48	71	0.65	0.14
96	0.08	67	3.21	96	0.79	0.22
121	0.09	92	3.75	121	0.78	0.18
146	0.10	117	4.15	146	0.82	0.20
171	0.11	142	4.47	171	0.80	0.22
196	0.13	167	4.76	196	0.86	0.24
221	0.12	192	5.00	221	0.79	0.24
246	0.10	281	5.50	359	0.72	0.27
271	0.13			455	0.82	0.26
				551	0.85	0.29
				647	0.80	0.35
				743	0.83	0.35
				839	0.72	0.35
				935	0.73	0.35
				1175	0.76	0.36
				1295	0.65	0.31
				1391	0.66	0.33
				1511	0.67	0.29
				1697	0.65	0.27
				1847	0.70	0.34
				2011	0.63	0.25

APPENDIX III (CONT)

COUPON TIME	L-1	L-2	L-3	L-4	L-5	L-6	L-7	L-8	L-1*	L-3*
24	0.69	0.09	0.91	1.99	1.85	0.42	0.55	0.60		
48	4.55	0.09	2.16	4.44	3.81	0.45	1.58	1.78		
72	9.30	0.08	3.04	6.48	5.23	0.44	2.42	2.37		
96	9.72	0.09	4.15	10.41	8.26	0.50	3.45	3.06		
120	9.66	0.10	2.51	1.68	5.45	0.40	0.47	3.14		
144	2.81	0.11	2.75	5.55	5.70	0.40	3.23	3.23		
168	2.86	0.09	3.18	6.10	5.99	0.42	4.11	3.63		
192	3.09	0.08	3.20	6.27	6.05	0.39	3.89	4.09		
216	3.23	0.08	3.19	6.49	3.28	0.38	3.78	3.62		
230	3.17	0.08	3.06	6.47	6.34	0.36	3.91	3.64		
278	2.93	0.10	3.36	6.65	8.77	0.40	4.70	4.18		
302	2.88	0.08	3.18	6.59	9.23	0.39	4.73	4.23		
422	2.98	0.08	3.13	6.49	8.92	0.42	4.96	4.66		
496	2.93	0.08	3.18	6.57	8.73	0.43	4.80	4.33		
558	2.81	0.08	3.29	6.41	9.10	0.39	4.83	2.21		
620	2.92	0.08	3.00	5.37	8.12	0.44	2.48	2.24		
750	4.08	0.07	2.88	5.11	8.21	0.40	4.34	4.15		

APPENDIX III (CONT)

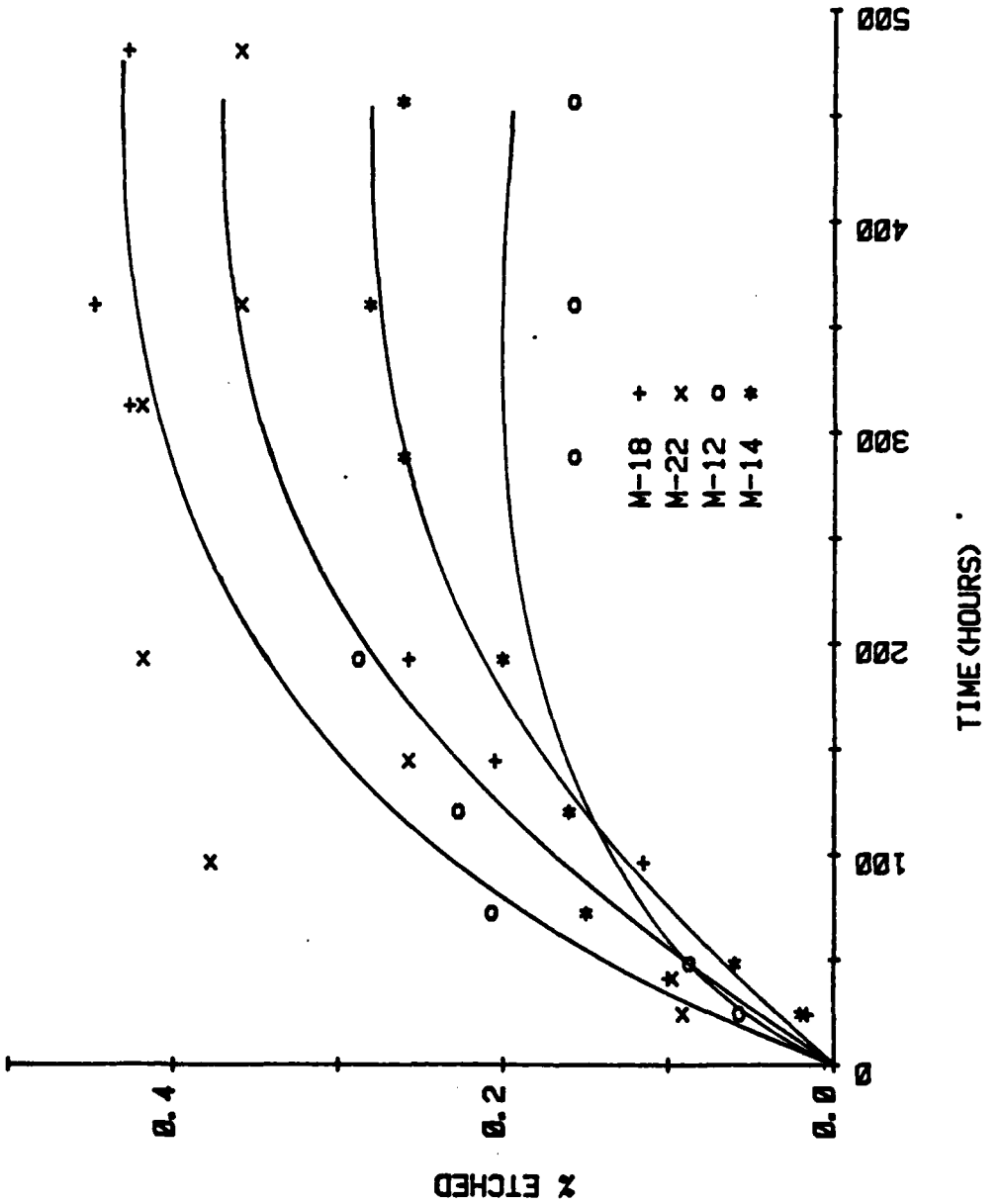
COUPON TIME	L-9	L-10	M-1	M-2	M-3	M-4	M-5	M-8	M-9	M-10
24	0.23	0.23	0.76	0.21	0.35	0.13	0.07	0.32	0.35	0.80
48	0.47	0.37	1.77	0.40	0.42	0.32	0.22	0.80	0.95	1.79
120	1.19	1.26	5.20	0.75	1.34	0.57	0.96	2.34	2.02	5.42
144	1.27	1.26	6.22	0.78	1.62	0.73	1.27	2.65	2.26	6.15
168	1.63	1.78	7.23	1.08	1.80	0.73	1.39	2.91	2.40	7.29
192	1.67	2.04	7.54	1.27	2.17	0.97	1.56	3.66	2.91	7.54
226	2.04	2.15	7.94	1.34	2.54	0.78	1.76	3.14	2.81	7.75
312	2.62	2.86	9.35	1.90	2.93	0.99	2.65	4.15	3.08	10.28
360	2.86	3.23	11.02	2.25	3.11	1.07	2.74	4.46	3.01	11.66
456	3.08	3.42	12.71	2.65	3.45	1.22	3.35	4.95	3.42	12.30

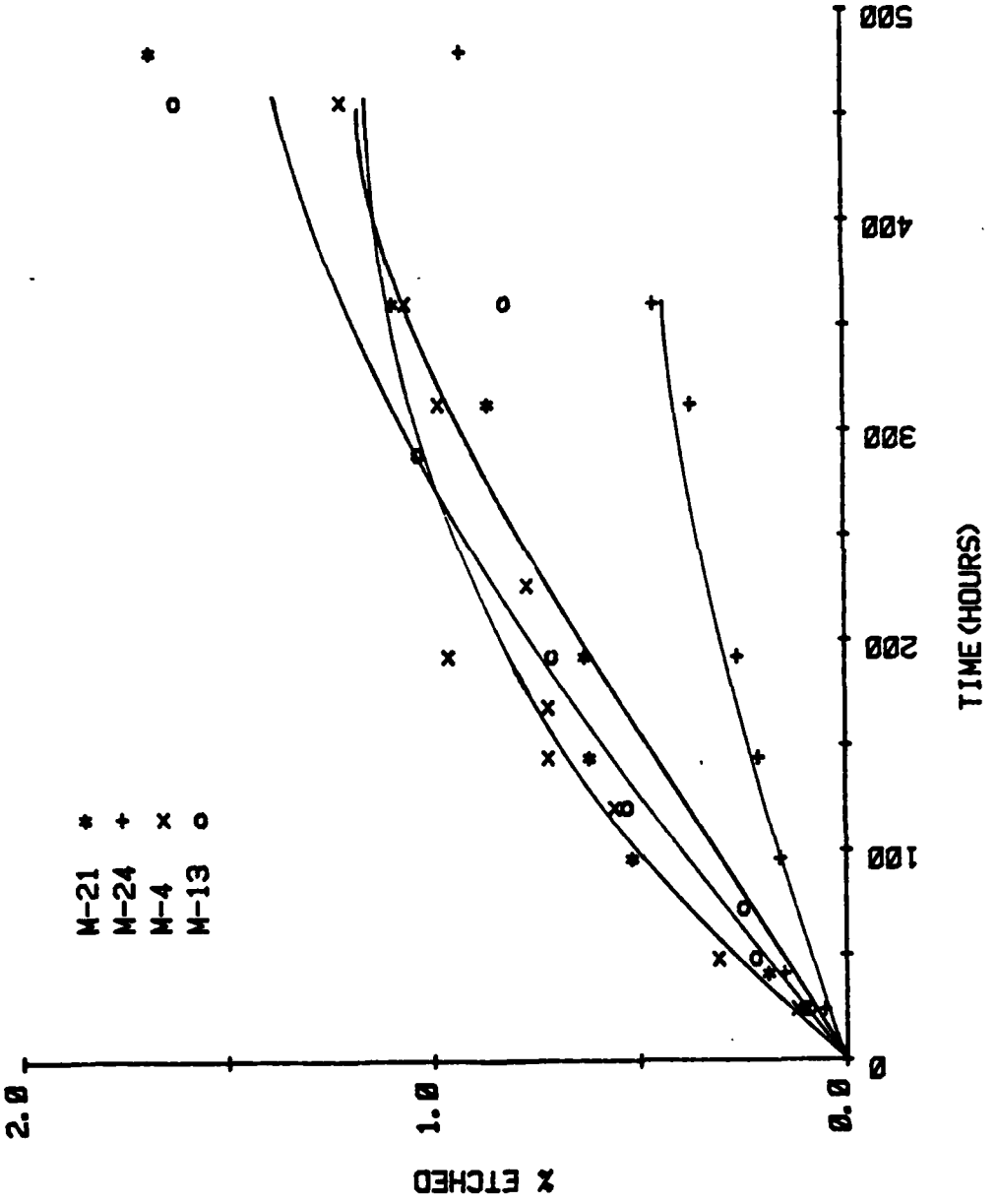
APPENDIX III (CONT)

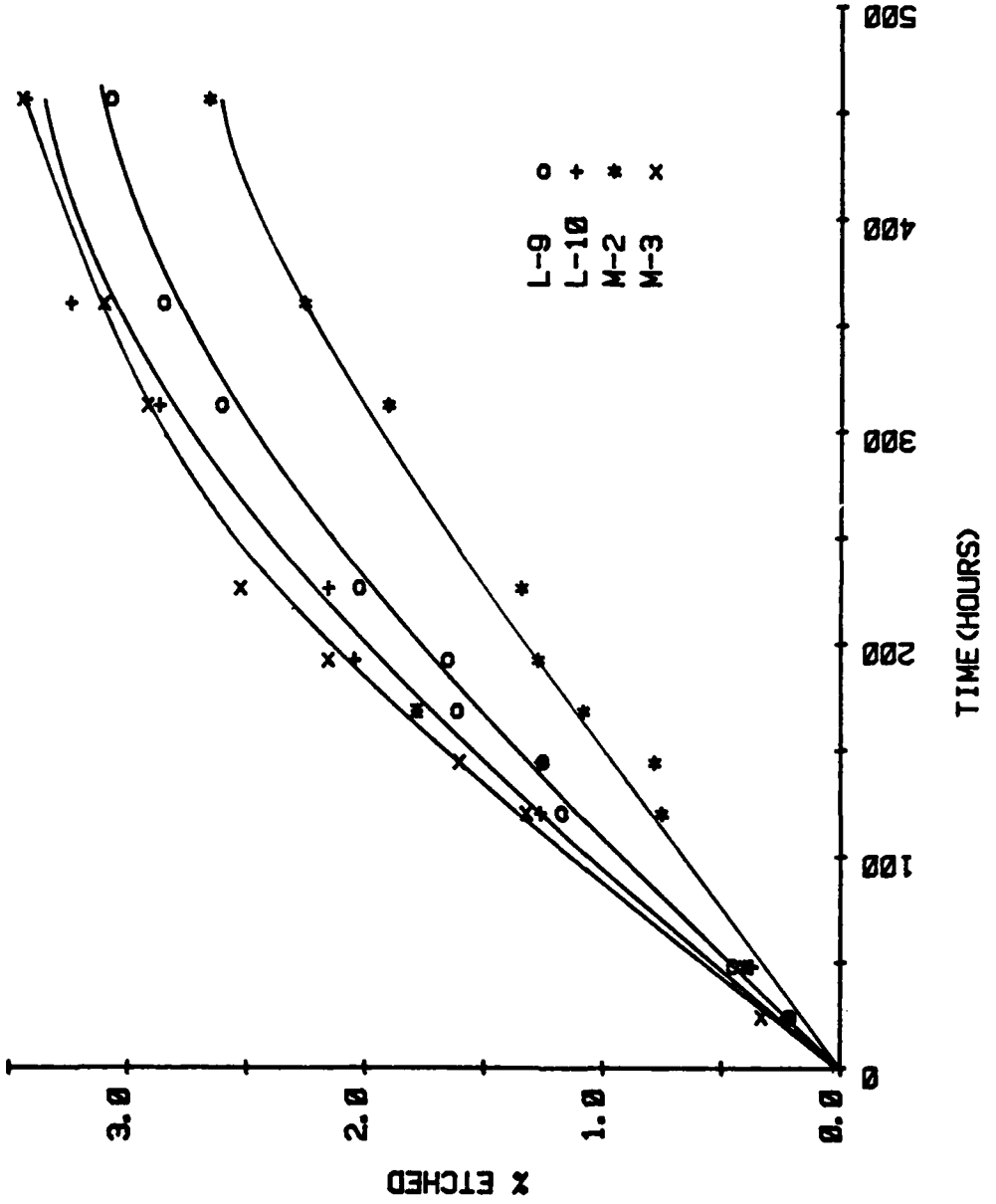
COUPON TIME	M-11	M-12	M-13	M-14	M-15	M-16	M-17
24	0.49	0.06	0.10	0.02	0.05	0.05	0.06
48	1.21	0.09	0.23	0.06	0.13	0.06	0.13
72	1.81	0.21	0.26	0.15	0.18	0.10	0.15
120	2.00	0.23	0.54	0.16	0.20	0.13	0.18
192	4.06	0.29	0.72	0.20	0.21	0.15	0.27
288	5.20	0.16	1.04	0.26	0.26	0.24	0.38
360	5.75	0.16	0.83	0.28	0.27	0.29	0.31
456	5.75	0.16	1.62	0.26	0.31	0.27	0.37
538	8.40	0.21	1.39	0.29	0.33	0.31	0.46

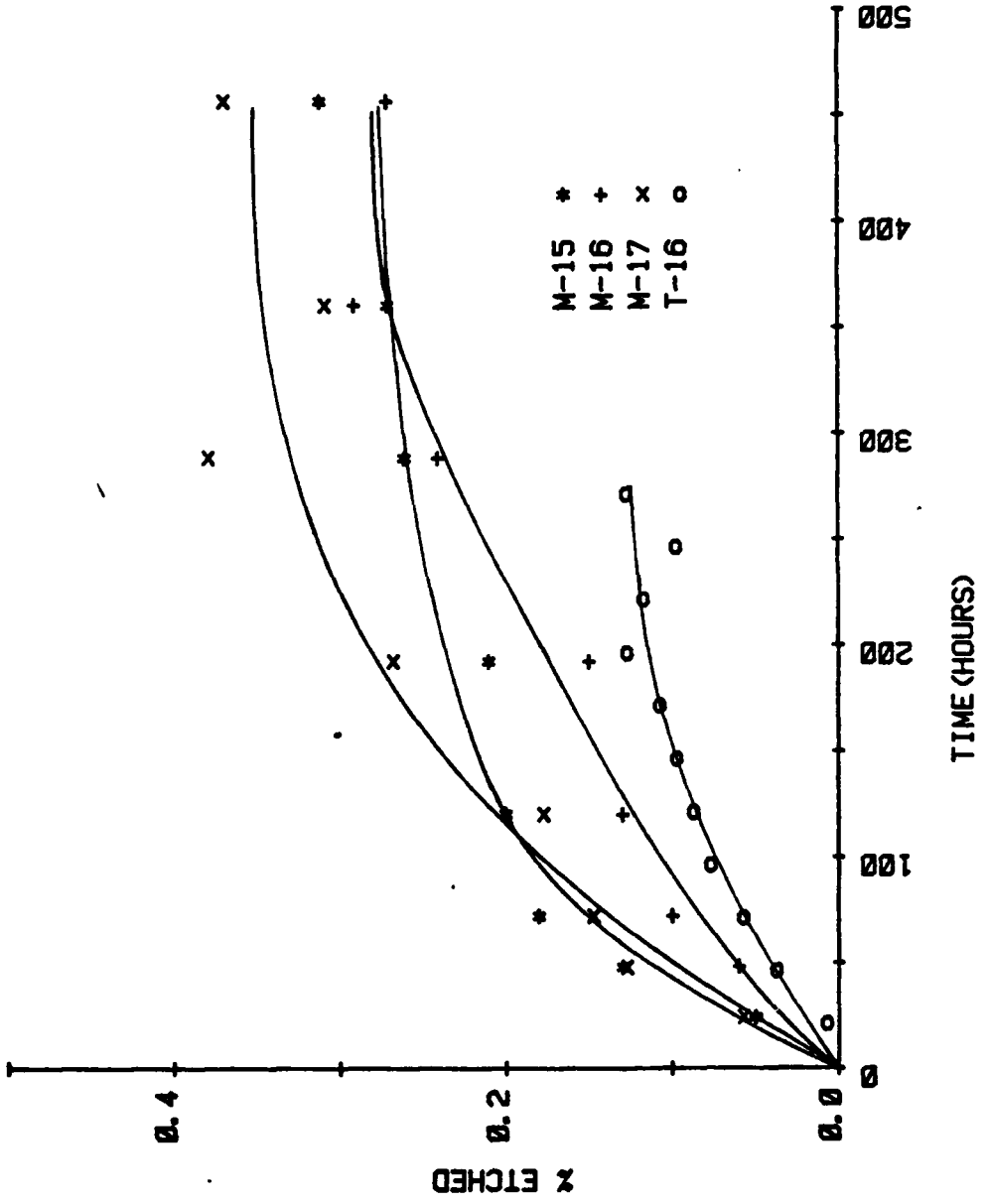
APPENDIX III (CONT)

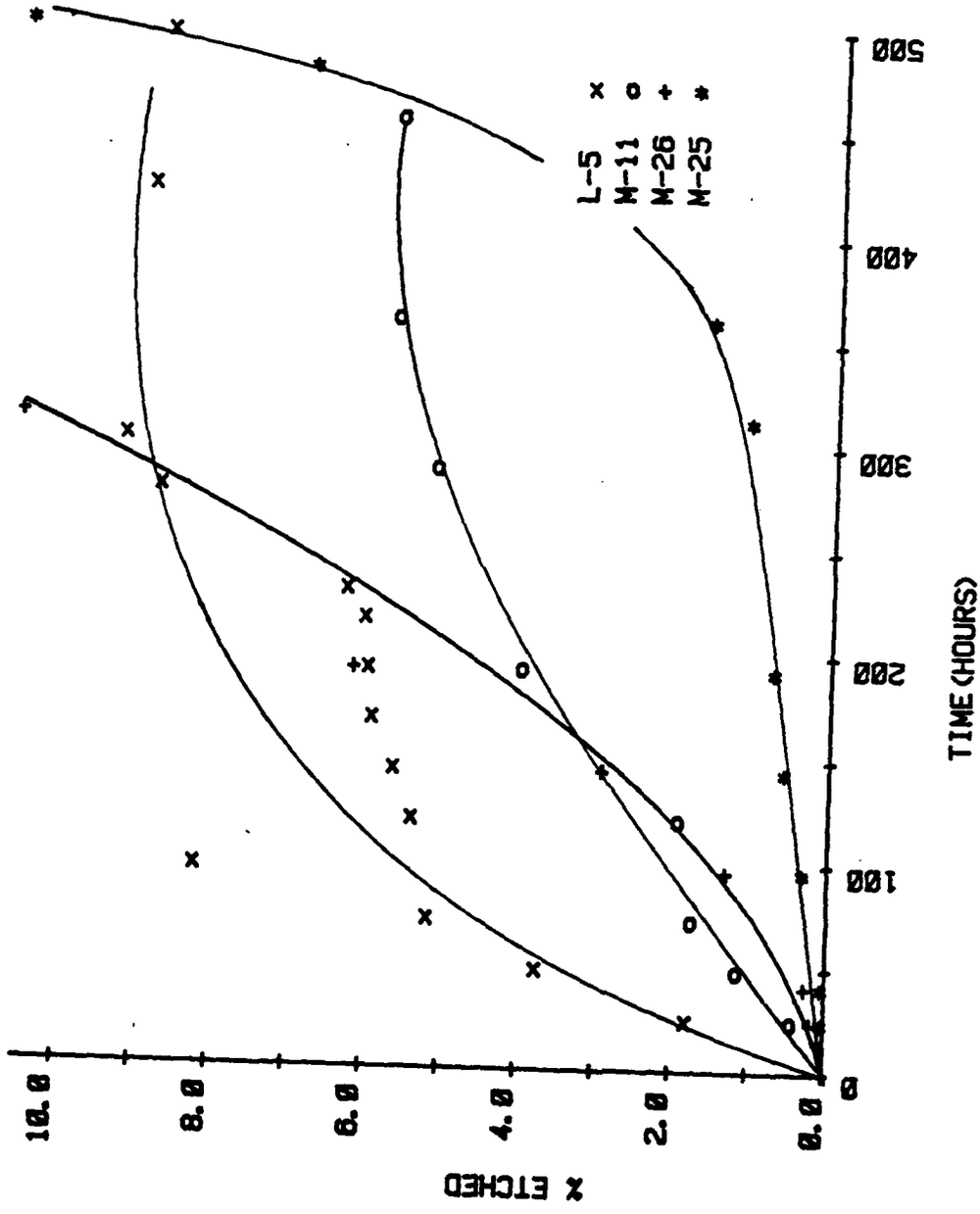
COUPON TIME	M-18	M-19	M-20	M-21	M-22	M-24	M-25	M-26	M-27	M-30
24	0.02	0.05	0.27	0.10	0.09	0.05	0.04	0.18	0.14	0.59
41	0.10	0.28	0.63	0.19	0.10	0.15	0.05	0.26	0.36	---
72	--	--	--	--	--	--	--	--	--	3.78
96	0.12	0.78	1.39	0.52	0.38	0.16	0.32	1.31	3.72	10.+
144	0.21	1.22	2.44	0.62	0.26	0.21	0.58	2.94	10.+	Test Stopped
192	0.26	1.57	3.14	0.63	0.42	0.26	0.74	6.18	Test Stopped	
312	0.43	2.59	4.71	0.86	0.42	0.37	1.11	10.+		
360	0.45	2.94	5.45	1.09	0.36	0.46	1.63	Test Stopped		
480	0.43	4.03	6.55	1.67	0.36	0.92	6.83			
528	0.42	4.25	7.08	1.78	0.38	1.30	10.49			

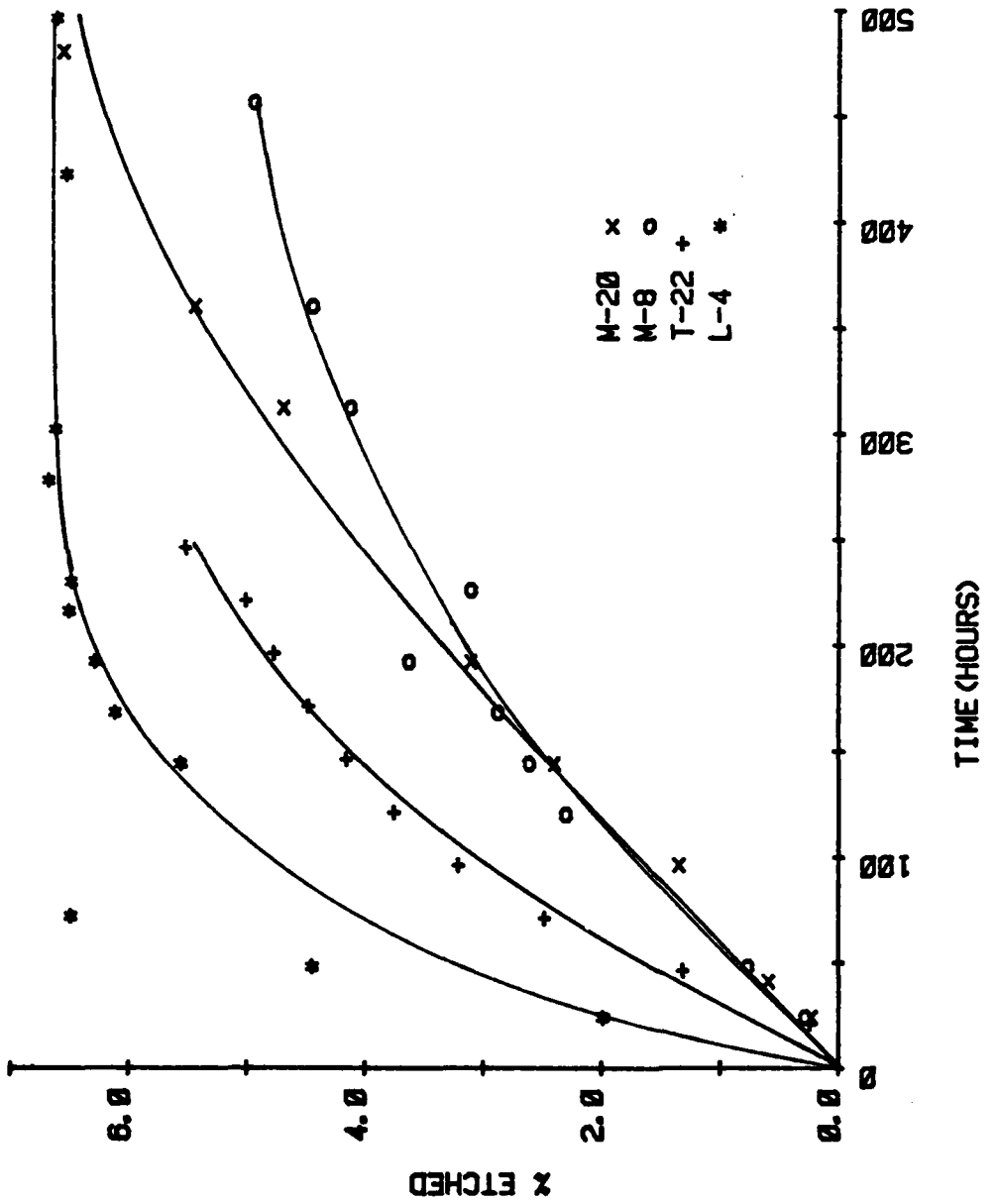

M-18 + x
M-22 x o
M-12 o *
M-14 *
0.0
0.2
0.4
% ETCHED
0
100
200
300
400
500
TIME (HOURS)

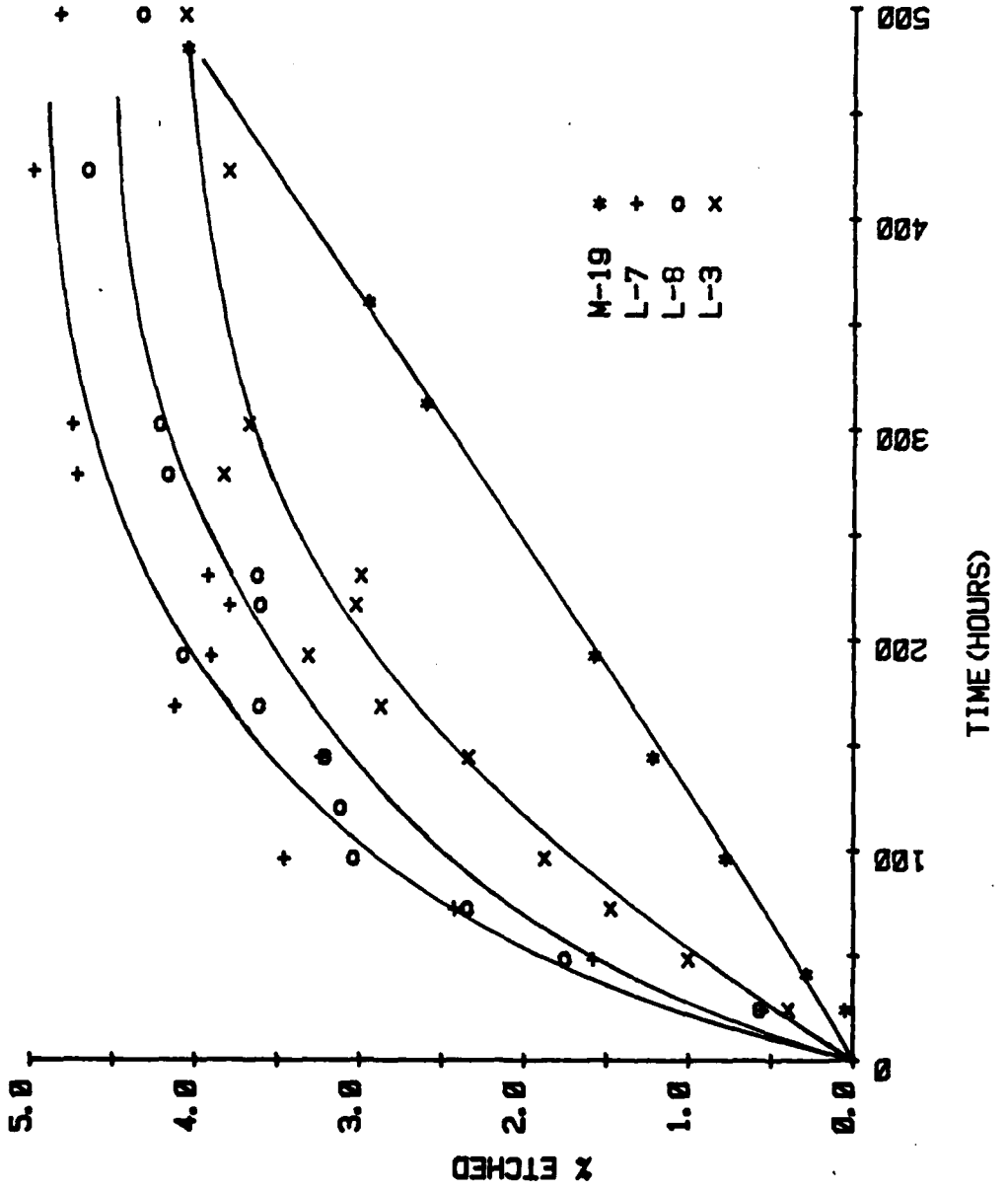

M-21
M-24
M-4
M-13
2.0
1.0
0.0
% ETCHED
0
100
200
300
400
500
TIME (HOURS)

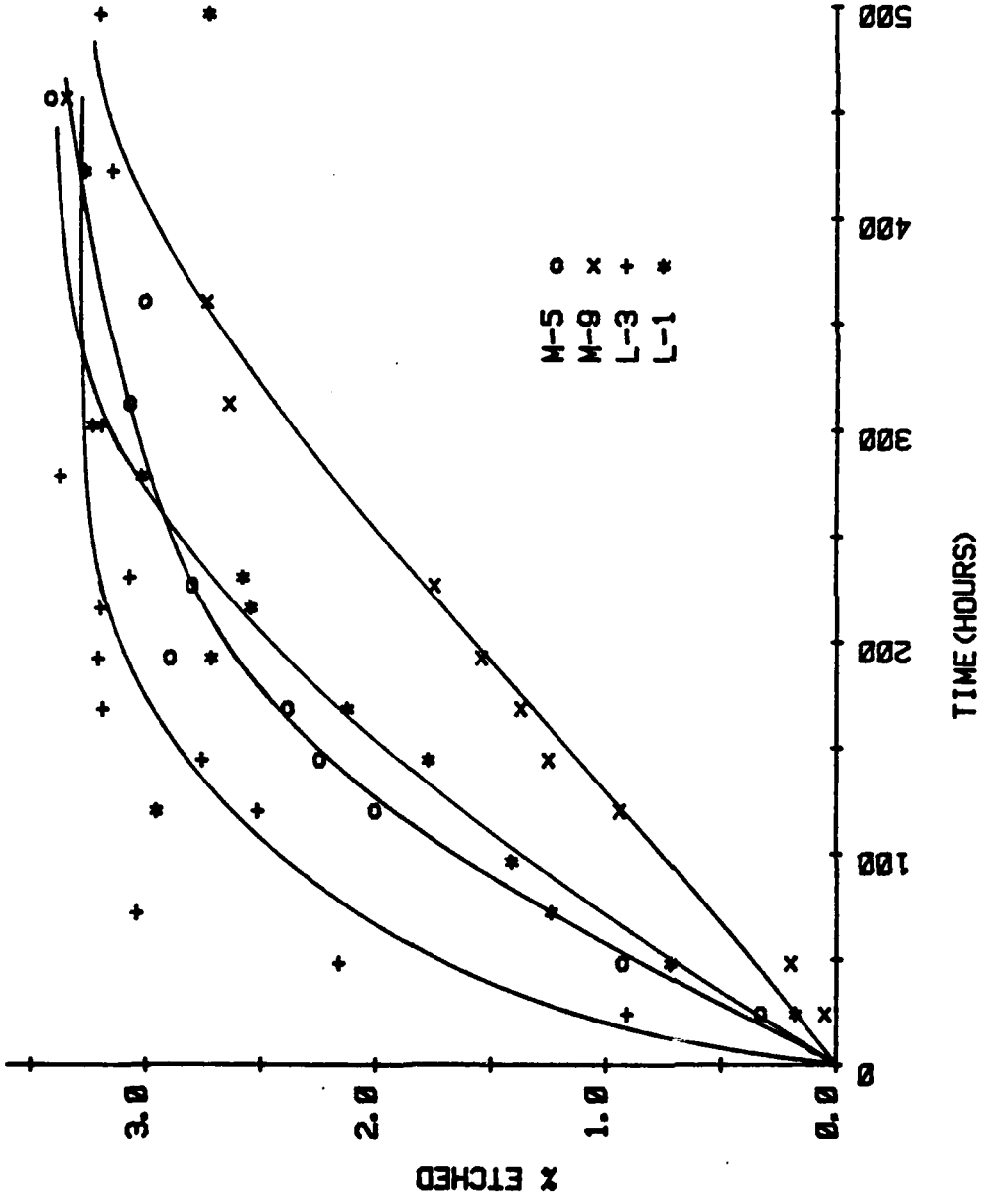

L-9
L-10
M-2
M-3
TIME (HOURS)
0
100
200
300
400
500
0.0
1.0
2.0
3.0
% ETCHED

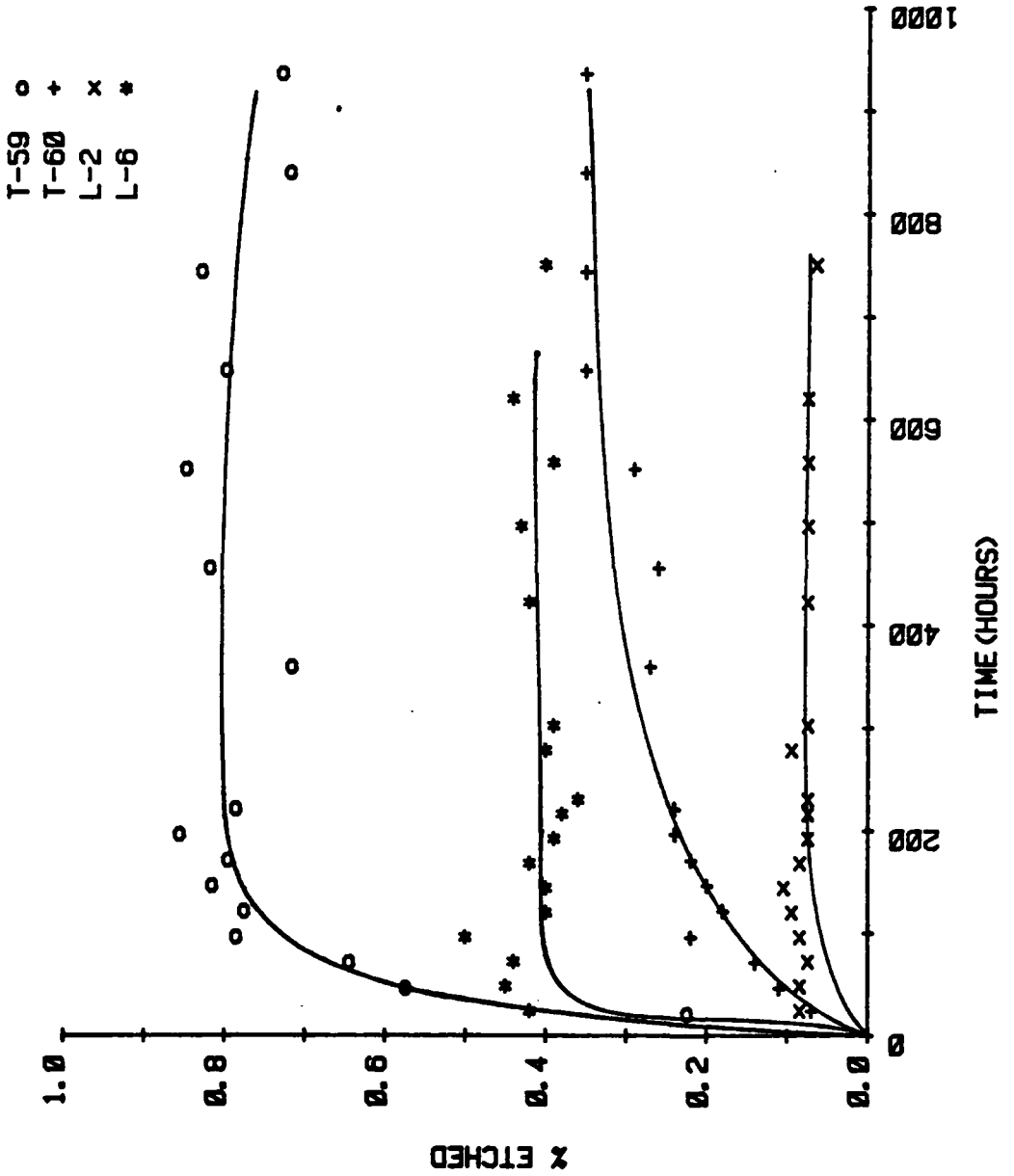

M-15 * + x o
M-16
M-17
T-16
% ETCHED
0.0
0.2
0.4
0
100
200
300
400
500
TIME (HOURS)

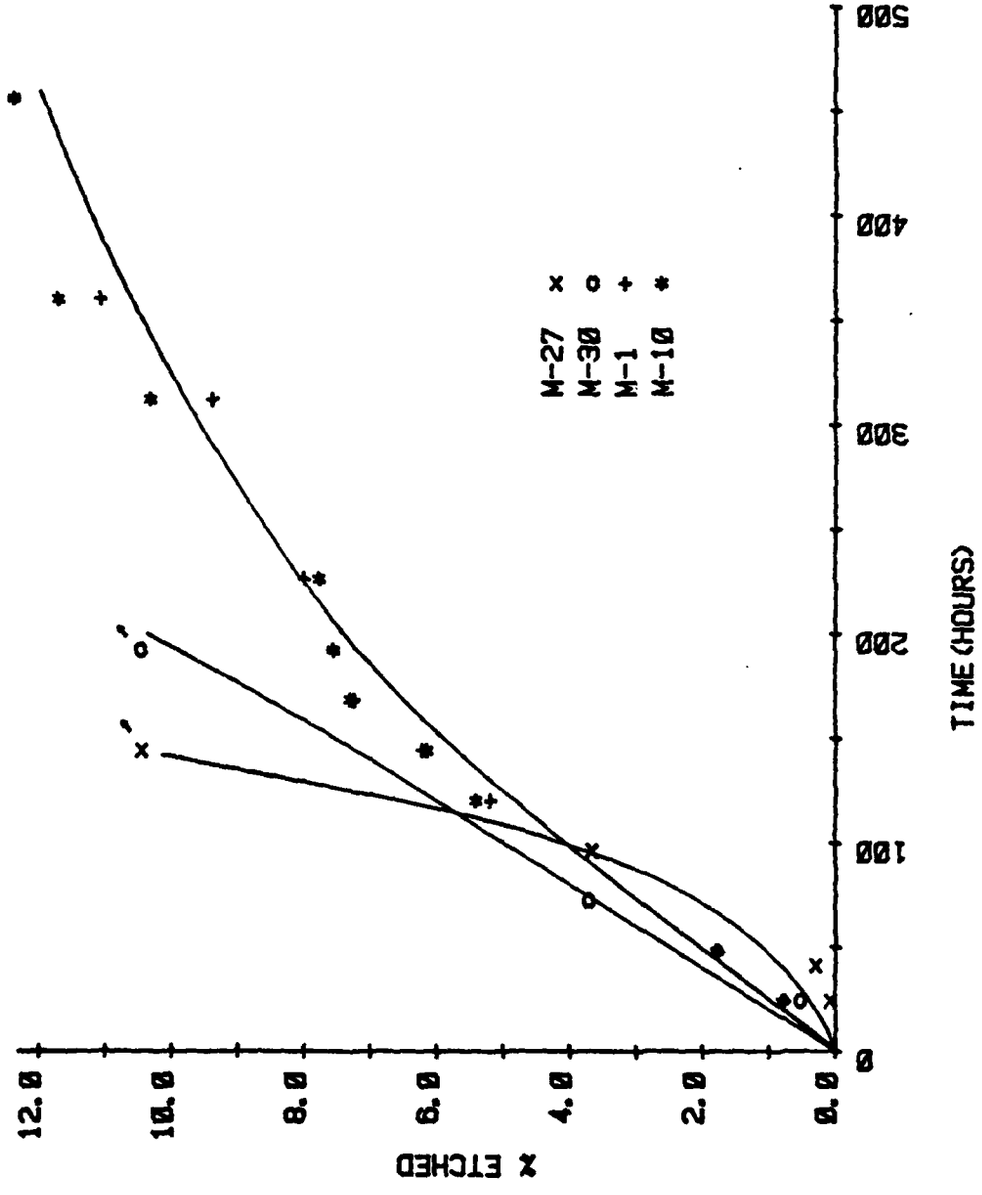

L-5
M-11
M-26
M-25
TIME (HOURS)
0
100
200
300
400
500
% ETCHED
0.0
2.0
4.0
6.0
8.0
10.0


M-20 x
M-8 o
T-22 +
L-4 *
0.0
2.0
4.0
6.0
% ETCHED
0
100
200
300
400
500
TIME (HOURS)


M-19
L-7
L-8
L-3
TIME (HOURS)
0
100
200
300
400
500
% ETCHED
0.0
1.0
2.0
3.0
4.0
5.0


M-5
M-9
L-3
L-1
TIME (HOURS)
0
100
200
300
400
500
% ETCHED
0.0
1.0
2.0
3.0


T-59 o
T-60 +
L-2 ×
L-6 *
1.0
0.8
0.6
0.4
0.2
0.0
X ETCHED
0
200
400
600
800
1000
TIME (HOURS)


M-27 x
M-30 o
M-1 +
M-10 *
X ETCHED
12.0
10.0
8.0
6.0
4.0
2.0
0.0
TIME (HOURS)
0
100
200
300
400
500

DISTRIBUTION LIST

Commander (12)
Defense Documentation Center
Cameron Station, Bldg. 5
ATTN: TISIA
Alexandria, VA 22314

Chief (1)
Research Development & Acquisition
Office, Deputy Chief of Staff
Department of the Army
Washington, DC 20310

Office of the Under Deputy Secretary (1) of
Defense (Research & Advanced Technology)
ATTN: ASST DIR, Electronics & Physical
Sciences
Washington, DC 20301

Director, Technical Information (1)
Advanced Research Projects Agency
1400 Wilson Blvd
Arlington, VA 22209

Commander (1)
U.S. Army Materiel Development
and Readiness Command
ATTN: DRCDE-D
5001 Eisenhower Avenue
Alexandria, VA 22333

Commander (1)
U.S. Army Tank-Automotive R&D Command
Technical Library, DRDTA-UL
Warren, MI 48090

Commander (1)
U.S. Army Electronics R&D Command
ATTN: DELET-PB
Fort Monmouth, NJ 07703

Commander (1)
U.S. Army Transportation Research &
Engineering Command
ATTN: Research Directorate
Fort Eustis, VA 23604

Technical Documents Center (2)
U.S. Army Mobility Equipment R&D Command
ATTN: DRDME-WC
Fort Belvoir, VA 22060

Chief (1)
Naval Ships Engineering Center
Department of the Navy
ATTN: Code 6157D, Mr. Albert Himy
Washington, DC 20362

Office Deputy Chief of Staff (1)
Research, Development and Engineering
ATTN: DAMA-CSS (Maj. Toch)
Washington, DC 20301

Department of the Navy (1)
Office of Naval Research
Ballston Tower #1
800 N. Quincy St. Code: 472, Rm. 624
Arlington, VA 22217

Commander (1)
Naval Ordnance Test Station
ATTN: Technical Library
China Lake, CA 93555

Commander (1)
Naval Electronics Laboratory Center
ATTN: Research Library
San Diego, CA 92152

Director (1)
U.S. Naval Research Laboratory
ATTN: Code 2027
Washington, DC 20390

Commander (1)
Aerospace Power Division
ATTN: AFAPL/PO (Mr. J. D. Reams)
Wright-Patterson Air Force Base
Dayton, OH 45443

Globe-Union, Inc. (1)
ATTN: Corporate Research
5757 North Green Bay Ave.
Milwaukee, WI 53210

Power Information Center (1)
Franklin Research Center
20th and Race Streets
Philadelphia, PA 19130

Director (1)
Lewis Research Center
Nat'l Aeronautics & Space Admin.
ATTN: Mr. H.J. Schwartz (M.S. 309-1)
21000 Brookpark Road
Cleveland, Ohio 44135

Dr. Paul Nelson, Director (1)
Argonne National Laboratory
Bldg 205
9700 South Cass Avenue
Argonne, IL 60439

Occidental Research Corporation (1)
ATTN: Herbert P. Silverman
P.O. Box 310, Dept. 2-K
LaVerne, CA 91750

U.S. Department of Energy (1)
Division of Fossil Fuel Utilization
Mail Station E-178, Germantown
Washington, DC 20545

Mr. Paul Milner (1)
Room 1D-259
Bell Telephone Laboratories
Murray Hill, NJ 07974

Gas Research Institute (1)
ATTN: Mr. Vincent Fiore
10 West 35th Street
Chicago, IL 60616

Engelhard Industries Division (1)
Engelhard Minerals & Chemicals Corp.
ATTN: V.A. Forlenza
Menlo Park, Edison, NJ 08817

Mr. George Ciprios (1)
Exxon Research & Engineering
P.O. Box 8
Linden, NJ 07036

General Electric Company (1)
50 Fordham Road
ATTN: L. J. Nuttall
Bldg. 1A
Wilmington, MA 01887

Power Systems Division (1)
United Technologies Corporation
ATTN: Al Meyer
PO Box 109
Governor's Highway
South Windsor, CT 06074

P.L. Howard Associates, Inc. (1)
Millington, MD 21561

Energy Research Corporation (1)
ATTN: Dr. B. S. Baker
3 Great Pasture Road
Danbury, CT 06810

Dr. S.B. Brummer (1)
Director of Physical Research
EIC, Inc.
55 Chapel Street
Newton, MA 02158

Electric Power Research Inst. (1)
ATTN: A.P. Fickett
P.O. Box 10412
Palo Alto, CA 94304

Dr. Ralph Roberts (1)
Energy Resources & Environmental
Systems Engineering
The MITRE Corporation
Mail Stop W-389
Westgate Research Park
McLean, VA 22101

Universal Oil Products, Inc. (1)
Ten UOP Plaza
ATTN: Stephen N. Massie
Government Contract Administrator
Des Plains, IL 60016

Technology Center (1)
ESB Incorporated
19 W. College Avenue
ATTN: Dr. D. T. Ferrell, Jr.
Yardley, PA 19067

Dr. Jose Giner (1)
Giner, Inc.
14 Spring Street
Waltham, MA 02154

Massachusetts Inst. of Technology (1)
ATTN: Professor H.P. Meissner
Cambridge, MA 02138

Dr. R. T. Foley (1)
Chemistry Department
The American University
Washington, DC 20016

Defense Research Establishment (1)
ATTN: E. Criddle
Ottawa, Ontario, Canada KIA024

State University of New York (1)
at Buffalo
ATTN: Professor Stanley Bruckenstein
Chemistry Department
Acheson Hall, SUNY/AB
Buffalo, NY 14214

Dr. Paul Stonehart (1)
Stonehart Associates, Inc.
34 Five Fields Road
Madison, CT 06443

DOD Proj. Manager-Mobile Elec. Power (1)
ATTN: DRCPM-MEP-TM (Glynn Burchette)
7500 Backlick Road
Springfield, VA 22150